WORLD INTELLECTUAL PROPERTY ORGANIZATION International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6: C07D 401/04, A01N 43/54, 43/58, 43/56, 43/50, 43/653

(11) International Publication Number:

WO 99/52893

(43) International Publication Date:

21 October 1999 (21.10.99)

(21) International Application Number:

PCT/EP99/02313

A₁

(22) International Filing Date:

6 April 1999 (06.04.99)

(30) Priority Data:

840/98

8 April 1998 (08.04.98)

CH

- (71) Applicant (for all designated States except AT US): NOVAR-TIS AG [CH/CH]; Schwarzwaldallee 215, CH-4058 Basel (CH).
- (71) Applicant (for AT only): NOVARTIS-ERFINDUNGEN VER-WALTUNGSGESELLSCHAFT MBH [AT/AT]; Brunner Strasse 59, A-1235 Vienna (AT).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): NEBEL, Kurt [CH/CH]; Baselweg 32, CH-4146 Hochwald (CH). KUNZ, Walter [CH/CH]; Buchenstrasse 9, CH-4104 Oberwil (CH). WENGER, Jean [CH/CH]; Zwischen den Rainen 374, CH-4323 Wallbach (CH).
- (74) Agent: BECKER, Konrad; Novartis AG, Corporate Intellectual Property, Patent & Trademark Dept., CH-4002 Basel (CH).

(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG. KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: N-PYRIDONYL HERBICIDES

(57) Abstract

Compounds of formula (I), wherein R₁ is hydrogen, fluorine, chlorine, bromine or methyl; R₂ is C₁-C₄alkyl, C₁-C₄haloalkyl, halogen, nitro, amino, cyano or R430-; R3 is as in claim 1; X1 is oxygen or sulfur; W is a group (W1), (W2), (W3), (W4), (W6), (W6), (W7), (W8), (W9) or (W10); and R8 to R32, R43 and X2 to X15 are defined in claim 1, and the agrochemically acceptable salts and stereoisomers of such compounds of formula (I), are suitable for use as herbicides.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	ТJ	Tajikistan
\mathbf{BE}	Belgium	GN	Guinea	MK	The former Yugoslav	TM	Turkmenistan
BF	Burkina Faso	GR	Greece		Republic of Macedonia	TR	Turkey
\mathbf{BG}	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	zw	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's	NZ	New Zealand		
CM	Cameroon		Republic of Korea	PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
\mathbf{CZ}	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

N-PYRIDONYL HERBICIDES

The present invention relates to novel, herbicidally active substituted N-pyridonyl nitrogen heterocycles, to processes for the preparation thereof, to compositions comprising those compounds, and to the use thereof in the control of weeds, especially in crops of useful plants, for example cereals, maize, rice, cotton, soybeans, rape, sorghum, sugar cane, sugar beet, sunflowers, vegetables, plantation crops and fodder plants, or in the inhibition of plant growth, and also in the non-selective control of weeds.

N-Pyridyl-pyrazoles and N-pyridyl-tetramethylenetriazolidine-dione compounds having herbicidal activity are described, for example, in DE-A-3 917 469, DE-A-19 518 054, DE-A-19 530 606 and US-A-5 306 694.

N-(2-Pyridyl)-pyridazinone compounds having herbicidal activity are described, for example, in JP-A-58-213 776.

Novel N-pyridonyl nitrogen heterocycles having herbicidal and growth-inhibiting properties have now been found.

The present invention therefore relates to compounds of formula I

$$R_2$$
 N
 N
 N
 N
 N
 N

wherein

R₁ is hydrogen, fluorine, chlorine, bromine or methyl;

R₂ is C₁-C₄alkyl, C₁-C₄haloalkyl, halogen, nitro, amino, cyano or R₄₃O-;

R₄₃ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, C₃-C₆cycloalkyl, C₁-C₈haloalkyl, cyano-C₁-C₈alkyl, C₃-C₈haloalkenyl, hydroxy-C₁-C₄alkyl, C₁-C₄alkoxy-C₁-C₄alkyl, C₃-C₆-alkenyloxy-C₁-C₄alkyl, C₃-C₆alkynyloxy-C₁-C₄alkyl, C₁-C₄alkoxy-C₁-C₄alkoxy-C₁-C₄alkyl, C₁-C₄alkyl, C₁-C₈alkylcarbonyl, C₁-C₈alkoxycarbonyl, C₃-C₈alkenyloxycarbonyl, benzyloxy-C₁- or -C₂-alkyl, benzylcarbonyl, benzyloxycarbonyl, phenyl, phenyl-C₂-C₈alkyl, benzyl, pyridyl, pyrimidinyl, pyrazinyl or pyridazinyl, those aromatic

and heteroaromatic rings being unsubstituted or mono- to tri-substituted by halogen, C_1 - C_4 alkyl or by C_1 - C_4 haloalkyl; or

$$R_{44}X_{16}C(O)\text{-}[C_1\text{-}C_8\text{alkylene}]\text{-}$$

$$R_{43} \text{ is } R_{44}X_{16}C(O)\text{-}C_1\text{-}C_8\text{alkyl- or } \qquad \qquad | \qquad \qquad | \qquad \qquad ;$$

$$(C_6H_5)$$

 X_{16} is oxygen, sulfur or $R_{\overline{45}} N -$;

- R₄₄ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, C₃-C₆cycloalkyl, C₁-C₈haloalkyl, C₃-C₈haloalkenyl, C₁-C₄alkyl, C₃-C₆alkenyloxy-C₁-C₄alkyl, C₁-C₄alkylthio-C₁-C₄alkyl, phenyl, phenyl mono- to tri-substituted by halogen, C₁-C₄alkyl or by C₁-C₄-haloalkyl, benzyl or benzyl mono- to tri-substituted on the phenyl ring by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl;
- R₄₅ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, C₃-C₆cycloalkyl, C₁-C₈haloalkyl or benzyl;
- R₃ is hydroxy, C₁-C₆alkoxy, C₃-C₆alkenyloxy, C₃-C₆alkynyloxy, C₁-C₆haloalkoxy, C₃-C₆haloalkoxy, C₃-C₆haloalkenyloxy, C₁-C₆alkoxy-C₁-C₆alkyl, C₃-C₆alkynyloxy-C₁-C₆alkyl, C₁-C₆alkoxy-C₁-C₆alkoxy-C₁-C₆alkyl, B₁-C₁-C₆alkoxy, R₄(R₅)N-, C₁-C₆alkyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₂-C₆haloalkyl, C₃-C₆haloalkenyl, C₃-C₆cycloalkyl, C₃-C₆haloalkyl, B₁-C₁-C₆alkyl, OHC-, C₁-C₆alkylcarbonyl, C₁-C₆alkylcarbonyl, C₁-C₆alkyl-S(O)₂-, C₆haloalkylcarbonyl, C₂-C₆alkenylcarbonyl, C₁-C₆alkyl-S(O)₂-,

$$C_1-C_6 \\ haloalkyl-S(O)_2-, \ C_3-C_8 \\ trialkylsilyloxy, \ (C_1-C_6 \\ alkyl)_2 \\ N-N=CH-, \quad \bigcirc \\ CH_2- \quad , \\ CH$$

hydroxyalkyl)- CH_2 -, (B_1 - C_1 - C_5 haloalkyl)- CH_2 -, (hydroxy- C_1 - C_5 alkyl)-O- or (B_1 - C_1 - C_5 -hydroxyalkyl)-O-;

B₁ is cyano, OHC-, HOC(O)-, C₁-C₆alkylcarbonyl, C₁-C₆haloalkylcarbonyl, C₁-C₆alkoxy-carbonyl, C₃-C₆alkenyloxycarbonyl, C₃-C₆alkynyloxycarbonyl, benzyloxy, benzyloxy-carbonyl, benzyloxycarbonyl mono- to tri-substituted on the phenyl ring by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl, benzylthio, benzylthiocarbonyl, benzylthiocarbonyl mono- to tri-substituted on the phenyl ring by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl, C₁-C₆haloalkoxycarbonyl, C₁-C₆alkylthio-C(O)-, R₆(R₇)NC(O)-, phenyl, phenyl mono- to

tri-substituted by halogen, C_1 - C_4 alkyl or by C_1 - C_4 haloalkyl, C_1 - C_6 alkyl- $S(O)_2$ -, C_1 - C_6 -alkyl-S(O)-, C_1 - C_6 alkylthio-, C_3 - C_6 cycloalkyl, C_1 - C_6 alkoxy, C_3 - C_6 alkenylthio;

R₄ and R₅ are each independently of the other hydrogen, C₁-C₆alkyl, C₃-C₆alkenyl, C₃-C₆-alkynyl, C₁-C₆haloalkyl, C₃-C₆haloalkenyl, C₃-C₆cycloalkyl, C₁-C₆alkoxy-C₁-C₆alkyl, OHC-, C₁-C₆alkylcarbonyl, C₁-C₆haloalkylcarbonyl, C₁-C₆alkyl-S(O)₂- or C₁-C₆haloalkyl-S(O)₂-;

R₆ and R₇ are each independently of the other hydrogen, C₁-C₆alkyl, C₃-C₆alkenyl, C₃-C₆-alkynyl, C₁-C₆haloalkyl, C₃-C₆haloalkenyl, phenyl, phenyl mono- to tri-substituted by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl, benzyl or benzyl mono- to tri-substituted on the phenyl ring by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl;

X₁ is oxygen or sulfur;

W is a group
$$R_{10}$$
 R_{10} R_{11} R_{11} R_{11} R_{11} R_{11} R_{11} R_{12} R_{13} R_{14} R_{14} R_{15} R_{14} R_{15} R_{14} R_{15} R_{16} R_{15} R_{16} R_{15} R_{16} R_{16} R_{15} R_{16} R_{16} R_{15} R_{14} R_{14} R_{15} R_{15} R_{10} R_{14} R_{15} R_{15} R_{10} R_{14} R_{15} R_{15} R_{15} R_{14} R_{15} R_{15} R_{16} R_{15} R_{16} R_{16}

R₈ is C₁-C₃alkyl, C₁-C₃haloalkyl or amino;

R₉ is C₁-C₃haloalkyl, C₁-C₃alkyl-S(O)_{n1}, C₁-C₃haloalkyl-S(O)_{n1} or cyano; or

R₈ and R₉ together form a C₃- or C₄-alkylene bridge or C₃- or C₄-alkenylene bridge, each of which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

n₁ is 0, 1 or 2:

R₁₀ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano; or

R₁₀ and R₉ together form a C₃- or C₄-alkylene bridge or C₃- or C₄-alkenylene bridge, each of which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

R₁₁ is hydrogen, C₁-C₃alkyl, halogen or cyano;

 R_{12} is C_1 - C_3 haloalkyl;

R₁₂ and R₁₁ together form a C₃- or C₄-alkylene bridge or C₃- or C₄-alkenylene bridge;

R₁₃ is hydrogen, C₁-C₃alkyl or halogen;

R₁₃ and R₁₂ together form a C₃- or C₄-alkylene bridge or C₃- or C₄-alkenylene bridge;

 R_{14} is hydrogen, C_1 - C_3 alkyl, halogen, C_1 - C_3 haloalkyl, R_{33} O-, R_{34} S(O)_{n2}, R_{35} (R₃₆)N,

 $R_{38}(R_{39})N-C(R_{37})=N-$, hydroxy, nitro or $N \equiv C-S-$;

 R_{33} is C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, C_2 - C_4 alkenyl, C_3 - or C_4 -alkynyl or C_1 - C_5 alkoxycarbonyl- C_1 - C_4 alkyl;

R₃₄ is C₁-C₄alkyl or C₁-C₄haloalkyl;

n₂ is 0, 1 or 2;

R₃₅ is hydrogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₃-C₆cycloalkyl, OHC- or C₁-C₄alkylcarbonyl;

R₃₆, R₃₇ and R₃₉ are each independently of the others hydrogen or C₁-C₄alkyl;

 R_{38} is C_1 - C_4 alkyl;

R₁₅ is hydrogen, C₁-C₄alkyl, halogen, C₁-C₄haloalkyl, C₂-C₄alkenyl, C₃-C₅haloalkenyl, C₃-or C₄-alkynyl, C₁-C₄alkoxy, C₁-C₄alkylcarbonyl, C₁-C₄haloalkylcarbonyl, C₂-C₄alkenylcarbonyl, C₂-C₄haloalkenylcarbonyl, C₂-C₄haloalkynylcarbonyl, C₁-C₄alkynylcarbonyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₃-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₃-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₃-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₃-C₄alkylcarbamoyl, C₃-C₄alkylcarbamoyl, C₃-C₄alkylcarbamoyl, C₃-C₄alkylcarbamoyl, C₃-C₄alkylcarbamoyl, C₃-C₄alkylcarbamoyl, C₃-C₄alkylcarbamoyl, C₃-C₄alkylcarbamoyl, C₃-C₄-alkylcarbamoylcarbamoyl, C₃-C₄-alkylcarbamoylcar

 n_3 is 0, 1 or 2;

R₁₆ and R₁₇ are each independently of the other hydrogen, C₁-C₄alkyl, halogen, C₁-C₄halo-alkyl or cyano;

R₁₈ and R₁₉ are each independently of the other hydrogen, methyl, halogen, hydroxy or =O;

R₂₀ and R₂₁ are each independently of the other hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl;

R₂₂ and R₂₃ are each independently of the other hydrogen, C₁-C₃alkyl, halogen or hydroxy;

R₂₄ and R₂₅ are each independently of the other hydrogen or C₁-C₄alkyl; or

 R_{24} and R_{25} together form the group $=C \begin{pmatrix} R_{40} \\ R_{41} \end{pmatrix}$

R₄₀ and R₄₁ are each independently of the other C₁-C₄alkyl; or

R₄₀ and R₄₁ together form a C₄- or C₅-alkylene bridge;

- R₂₆ is hydrogen or C₁-C₃alkyl; or
- R₂₆ together with R₂₅ forms a C₃-C₅alkylene bridge, which may be interrupted by oxygen and/or substituted by halogen, C₁-C₄alkyl, C₂-C₄alkenyl, C₁-C₃haloalkyl, C₁-C₃alkyl-carbonyloxy, C₁-C₄alkoxycarbonyl, C₁-C₃alkylsulfonyloxy, hydroxy or by =O;
- R_{27} , R_{28} , R_{29} and R_{30} are each independently of the others hydrogen, C_1 - C_3 alkyl, C_3 or C_4 -alkenyl or C_3 - C_5 alkynyl; or
- R₂₇ and R₂₈ together and/or R₂₉ and R₃₀ together in each case form a C₂-C₅alkylene bridge or C₃-C₅alkenylene bridge, each of which may be interrupted by oxygen, sulfur or S(O)₂- and/or substituted by halogen, C₁-C₄alkyl, C₂-C₄alkenyl, C₁-C₃alkylcarbonyloxy, C₁-C₃alkylsulfonyloxy, hydroxy or by =O;
- R₃₁ is hydrogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₃- or C₄-alkenyl, C₃- or C₄-haloalkenyl or C₃- or C₄-alkynyl;
- R₃₂ is hydrogen, C₁-C₄alkyl, C₁-C₃alkoxy-C₁- or -C₂-alkyl, C₁-C₄haloalkyl, C₃- or C₄-alkenyl, C₃- or C₄-haloalkenyl or C₃- or C₄-alkynyl; or
- R₃₂ and R₃₁ together form a C₃-C₅alkylene bridge; and
- X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , X_8 , X_9 , X_{10} , X_{11} , X_{12} , X_{13} , X_{14} and X_{15} are each independently of the others oxygen or sulfur,

and the agrochemically acceptable salts and stereoisomers of those compounds of formula I.

In the above definitions, halogen is to be understood as being iodine or, preferably, fluorine, chlorine or bromine.

The alkyl, alkenyl and alkynyl groups in the substituent definitions may be straight-chain or branched, this applying also to the alkyl, alkenyl and alkynyl moiety of the following groups: alkylcarbonyl, alkenylcarbonyl, alkynylcarbonyl, hydroxyalkyl, cyanoalkyl, alkoxyalkyl, alkoxyalkyl, alkoxyalkyl, alkylthio, alkynylthio, alkylthio-C(O)-, alkylsulfinyl, alkylsulfonyl, alkylaminocarbonyl, dialkylaminocarbonyl, (alkyl)₂N-N=CH-, alkylcarbamoyl, trialkylsilyloxy, B₁-alkyl and HOC(O)-alkyl.

Alkyl groups are, for example, methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl and the various isomeric pentyl and hexyl radicals. Methyl, ethyl, n-propyl, isopropyl and n-butyl are preferred.

Examples of alkenyl radicals that may be mentioned are vinyl, allyl, methallyl, 1-methylvinyl, but-2-en-1-yl, pentenyl and 2-hexenyl, with preference being given to alkenyl radicals

having a chain length of from 3 to 5 carbon atoms.

Examples of alkynyl radicals that may be mentioned are ethynyl, propargyl, 1-methyl-propargyl, 3-butynyl, but-2-yn-1-yl, 2-methylbutyn-2-yl, but-3-yn-2-yl, 1-pentynyl, pent-4-yn-1-yl and 2-hexynyl, with preference being given to alkynyl radicals having a chain length of from 2 to 4 carbon atoms.

Suitable haloalkyl radicals are alkyl groups that are mono- or poly-substituted, especially mono- to tri-substituted, by halogen, halogen being in particular iodine or especially fluorine, chlorine or bromine, for example fluoromethyl, difluoromethyl, trifluoromethyl, chloromethyl, dichloromethyl, trichloromethyl, 2-fluoroethyl, 2,2-difluoroethyl, 2-chloroethyl, 2,2-dichloroethyl, 2,2,2-trifluoroethyl, 2,2,2-trichloroethyl and pentafluoroethyl.

Suitable haloalkenyl radicals are alkenyl groups mono- or poly-substituted by halogen, halogen being in particular bromine, iodine or especially fluorine or chlorine, for example 2- or 3-fluoropropenyl, 2- or 3-chloropropenyl, 2- or 3-bromopropenyl, 2,3,3-trifluoropropenyl, 2,3,3-trichloropropenyl, 4,4,4-trifluorobut-2-en-1-yl and 4,4,4-trichlorobut-2-en-1-yl. Of the alkenyl radicals mono-, di- or tri-substituted by halogen, preference is given to those having a chain length of 3 or 4 carbon atoms. The alkenyl groups may be substituted by halogen at saturated or unsaturated carbon atoms.

Suitable haloalkynyl radicals are, for example, alkynyl groups mono- or poly-substituted by halogen, halogen being bromine, iodine or especially fluorine or chlorine, for example 3-fluoropropynyl, 3-chloropropynyl, 3-bromopropynyl, 3,3,3-trifluoropropynyl and 4,4,4-trifluoro-but-2-yn-1-yl.

Alkylthio is, for example, methylthio, ethylthio, propylthio or butylthio or a branched isomer thereof.

Alkylsulfonyl is, for example, methylsulfonyl, ethylsulfonyl, propylsulfonyl, isopropylsulfonyl, n-butylsulfonyl, isobutylsulfonyl, sec-butylsulfonyl, tert-butylsulfonyl or an isomer of pentylsulfonyl or hexylsulfonyl; preferably methylsulfonyl or ethylsulfonyl.

Haloalkylsulfonyl is, for example, fluoromethylsulfonyl, difluoromethylsulfonyl, trifluoromethylsulfonyl, chloromethylsulfonyl, trichloromethylsulfonyl, 2-fluoroethylsulfonyl, 2,2,2-trifluoroethylsulfonyl or 2,2,2-trichloroethylsulfonyl.

Cyanoalkyl is, for example, cyanomethyl, cyanoethyl, cyanoeth-1-yl or cyanopropyl. Hydroxyalkyl is, for example, hydroxymethyl, 2-hydroxyethyl or 3-hydroxypropyl. Alkylamino is, for example, methylamino, ethylamino or an isomer of propylamino or butylamino. Dialkylamino is, for example, dimethylamino, diethylamino or an isomer of dipropylamino or dibutylamino.

Alkenylamino is, for example, allylamino, methallylamino or but-2-en-1-ylamino.

Alkynylamino is, for example, propargylamino or 1-methylpropargylamino.

Haloalkylamino is, for example, chloroethylamino, trifluoroethylamino or 3-chloropropylamino.

Di(haloalkyl)amino is, for example, di(2-chloroethyl)amino.

Alkylcarbonyl is especially acetyl or propionyl.

Haloalkylcarbonyl is especially trifluoroacetyl, trichloroacetyl, 3,3,3-trifluoropropionyl or 3,3,3-trichloropropionyl.

Alkenylcarbonyl is especially vinylcarbonyl, allylcarbonyl, methallylcarbonyl, but-2-en-1-ylcarbonyl, pentenylcarbonyl or 2-hexenylcarbonyl.

Alkynylcarbonyl is especially acetylenecarbonyl, propargylcarbonyl, 1-methylpropargylcarbonyl, 3-butynylcarbonyl, but-2-yn-1-ylcarbonyl or pent-4-yn-1-ylcarbonyl.

Alkoxy is, for example, methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, isobutoxy, secbutoxy, tert-butoxy or an isomer of pentyloxy or hexyloxy.

Alkenyloxy is, for example, allyloxy, methallyloxy or but-2-en-1-yloxy.

Alkynyloxy is, for example, propargyloxy or 1-methylpropargyloxy.

Alkoxyalkyl is, for example, methoxymethyl, methoxyethyl, ethoxymethyl, ethoxyethyl, n-propoxymethyl, n-propoxyethyl, isopropoxymethyl or isopropoxyethyl.

Alkenyloxyalkyl is, for example, allyloxyalkyl, methallyloxyalkyl or but-2-en-1-yloxyalkyl.

Alkynyloxyalkyl is, for example, propargyloxyalkyl or 1-methylpropargyloxyalkyl.

Alkoxycarbonyl is, for example, methoxycarbonyl, ethoxycarbonyl, n-propoxycarbonyl, iso-propoxycarbonyl or n-butoxycarbonyl, preferably methoxycarbonyl or ethoxycarbonyl.

Alkenyloxycarbonyl is, for example, allyloxycarbonyl, methallyloxycarbonyl, but-2-en-1-yloxycarbonyl, pentenyloxycarbonyl or 2-hexenyloxycarbonyl.

Alkynyloxycarbonyl is, for example, propargyloxycarbonyl, 3-butynyloxycarbonyl, but-2-yn-1-yloxycarbonyl or 2-methylbutyn-2-yloxycarbonyl.

Haloalkoxy is, for example, fluoromethoxy, difluoromethoxy, trifluoromethoxy, 2,2,2-trifluoroethoxy, 1,1,2,2-tetrafluoroethoxy, 2-fluoroethoxy, 2-chloroethoxy or 2,2,2-trichloroethoxy. Suitable haloalkenyloxy radicals are alkenyloxy groups mono- or poly-substituted by halogen, halogen being in particular bromine, iodine or especially fluorine or chlorine, for example 2- or 3-fluoropropenyloxy, 2- or 3-chloropropenyloxy, 2- or 3-bromopropenyloxy, 2,3,3-trifluoropropenyloxy, 2,3,3-trifluoropropenyloxy, 2,3,3-trifluoropropenyloxy, 2,4,4,4-trifluoro-but-2-en-1-yloxy or

4,4,4-trichlorobut-2-en-1-yloxy.

The cycloalkyl radicals suitable as substituents are, for example, cyclopropyl, cyclobutyl, cyclopentyl and cyclohexyl.

The halocycloalkyl radicals suitable as substituents are, for example, mono-, di- or up to per-halogenated cycloalkyl radicals, for example fluorocyclopropyl, chlorocyclopropyl, bromocyclopropyl, 2,2-dichlorocyclopropyl, 2,2-difluorocyclopropyl, 2,2-dibromocyclopropyl, 2-fluoro-2-chlorocyclopropyl, 2-chloro-2-bromocyclopropyl, 2,2,3,3-tetrafluorocyclopropyl, 2,2,3,3-tetrachlorocyclopropyl, pentafluorocyclopropyl, fluorocyclobutyl, chlorocyclobutyl, 2,2-difluorocyclobutyl, 2,2,3,3-tetrafluorocyclobutyl, 2,2,3-trifluoro-3-chlorocyclobutyl, 2,2-dichloro-3,3-difluorocyclobutyl, fluorocyclopentyl, difluorocyclopentyl, chlorocyclopentyl, perfluorocyclopentyl, chlorocyclopexyl and pentachlorocyclohexyl.

Corresponding meanings may also be given to the substituents in combined definitions, such as, for example, alkylcarbonyloxy, alkoxyalkoxyalkyl, alkoxycarbonylalkyl, haloalkoxycarbonyl, haloalkylcarbonyl, haloalkenylcarbonyl, haloalkynylcarbonyl, alkylthio-C(O)-, alkenylthio, alkynylthio, alkyl-S(O)-, alkylsulfonyloxy, $R_{33}O$ -, $R_4(R_5)N$ -, $R_{35}(R_{36})N$ -, $R_6(R_7)NC(O)$ -, $R_{38}(R_{39})N$ -C(R_{37})=N-, $R_{34}S(O)_{n2}$, R_{1} -alkyl, R_{1} -alkoxy, R_{1} -CH=N-, (R_{1} -haloalkyl)-CH₂- and (R_{1} -hydroxyalkyl)-CH₂-.

In the definition of R₃, (C₁-C₅hydroxyalkyl)-CH₂-, (B₁-C₁-C₅hydroxyalkyl)-CH₂- and (B₁-C₁-C₅haloalkyl)-CH₂- signify that only the C₁-C₅alkyl moiety is hydroxylated or halogenated, that is to say the methylene group is not hydroxylated or halogenated. L in the reagents of formulae VI, XI, XIX, XXVIII, XXXIa, XXXIb and XXXXII denotes a leaving group, such as, for example, halogen, preferably chlorine, bromine or iodine,

$$C_1$$
- C_3 alkyl- or aryl-sulfonyloxy, preferably CH_3SO_2O - or CH_3 C_2O - , or

C₁-C₆alkylcarbonyloxy, preferably acetyloxy.

L₁ in the reagent of formula XX denotes a leaving group, such as, for example, HOS(O)₂O₋.

$$NO_2$$
 or H_3C $OS(O)_2$.

L₂ in the reagents of formulae XXXIIa and XXXIIc denotes a leaving group, such as, for example, hydroxy, C₁-C₄alkoxy or halogen, preferably chlorine, bromine or iodine.

 L_3 in the reagent of formula XXXVIII denotes a leaving group, such as, for example, chlorine or bromine, trichloromethoxy or -N.

In the definitions of cyanoalkyl, alkylcarbonyl, alkylcarbonyloxy, alkenylcarbonyl, haloalkenylcarbonyl, alkynylcarbonyl, alkoxycarbonyl, alkylthiocarbonyl and haloalkylcarbonyl, the upper and lower limits of the number of carbon atoms given in each case do not include the cyano or carbonyl carbon atom, as the case may be. The invention relates also to the salts that the compounds of formula I having azide hydrogen, especially the derivatives with carboxylic acid and sulfonamide groups (e.g. carboxyl-substituted alkyl and alkoxy groups and alkyl-S(O)₂NH and haloalkyl-S(O)₂NH groups) are able to form with bases. Those salts are, for example, alkali metal salts, e.g. sodium and potassium salts; alkaline earth metal salts, e.g. calcium and magnesium salts; ammonium salts, that is to say unsubstituted ammonium salts and mono- or poly-substituted ammonium salts, e.g. triethylammonium and methylammonium salts; or salts with other organic bases.

Among the alkali metal and alkaline earth metal hydroxides as salt formers, attention is drawn, for example, to the hydroxides of lithium, sodium, potassium, magnesium and calcium, but especially to the hydroxides of sodium and potassium. Suitable salt formers are described, for example, in WO 97/41112.

Examples of amines suitable for ammonium salt formation include ammonia as well as primary, secondary and tertiary C₁-C₁₈alkylamines, C₁-C₄hydroxyalkylamines and C₂-C₄-alkoxyalkylamines, for example methylamine, ethylamine, n-propylamine, isopropylamine, the four isomers of butylamine, n-amylamine, isoamylamine, hexylamine, heptylamine, octylamine, nonylamine, decylamine, pentadecylamine, hexadecylamine, heptylamine, octadecylamine, methylethylamine, methylisopropylamine, methylhexylamine, methylnonylamine, methylpentadecylamine, methyloctadecylamine, ethylbutylamine, ethylheptylamine, ethyloctylamine, diethylamine, di-n-propylamine, hexylheptylamine, hexyloctylamine, dimethylamine, diethylamine, din-propylamine, diisopropylamine, di-n-butylamine, di-n-amylamine, diisoamylamine, dihexylamine, diheptylamine, dioctylamine, ethanolamine, n-propanolamine, isopropanolamine, N,N-diethanolamine, N-ethylpropanolamine, N-butylethanolamine, allylamine, n-butenyl-2-amine, n-pentenyl-2-amine, 2,3-dimethylbutenyl-2-amine, dibutenyl-2-amine, n-hexenyl-2-amine, propylenediamine, trimethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-sec-butylamine, tri-n-amylamine,

methoxyethylamine and ethoxyethylamine; heterocyclic amines, for example pyridine, quinoline, isoquinoline, morpholine, thiomorpholine, piperidine, pyrrolidine, indoline, quinuclidine and azepine; primary arylamines, for example anilines, methoxyanilines, ethoxyanilines, o-, m- and p-toluidines, phenylenediamines, benzidines, naphthylamines and o-, m- and p-chloroanilines; but especially triethylamine, isopropylamine and diisopropylamine.

The salts of compounds of formula I having basic groups, especially having basic pyrazolyl rings (W_3 , W_4), or the derivatives with amino groups, for example alkylamino and dialkylamino groups, in the definition of R_3 , R_8 or R_{14} are, for example, salts with inorganic or organic acids, for example hydrohalic acids, such as hydrofluoric acid, hydrochloric acid, hydrobromic acid or hydriodic acid, and also sulfuric acid, phosphoric acid and nitric acid, and organic acids, such as acetic acid, trifluoroacetic acid, trichloroacetic acid, propionic acid, glycolic acid, thiocyanic acid, citric acid, benzoic acid, oxalic acid, formic acid, benzenesulfonic acid, p-toluenesulfonic acid and methanesulfonic acid.

The presence of an asymmetric carbon atom in the compounds of formula I, e.g. in the substituent R_3 where R_3 is a branched alkyl, alkenyl, haloalkyl or alkoxyalkyl group or R_3 is $(B_1-C_1-C_5\text{hydroxyalkyl})-CH_2$ -, wherein e.g. B_1 is $C_1-C_6\text{alkyl}-S(O)$ -, means that the compounds may be in the form of optically active individual isomers or in the form of racemic mixtures. In the present invention, "compounds of formula I" is to be understood as including both the pure optical antipodes and the racemates or diastereoisomers. When an aliphatic C=C or C=N-O double bond (syn/anti) is present, geometric isomerism may occur. The present invention relates to those isomers also.

Preference is given to compounds of formula lo

$$R_2$$
 N
 N
 N
 N
 N
 N

wherein

 R_1 is hydrogen, fluorine, chlorine, bromine or methyl; R_2 is methyl, halogen, hydroxy, nitro, amino or cyano; and R_3 , X_1 and W are as defined for formula I.

Preference is also given to compounds of formula I wherein W is the group

compounds, special preference is given to those wherein R_8 is methyl; R_9 is trifluoromethyl; R_{10} is hydrogen; and X_2 and X_3 are oxygen.

Also preferred are compounds of formula I wherein W is a group

$$R_{13}$$
 R_{11}
 R_{11}
 R_{11}
 R_{26}
 R_{25}
 R_{24}
 R_{32}
 R_{31}
 R_{31}
 R_{31}
 R_{31}
 R_{32}
 R_{31}
 R_{31}
 R_{32}
 R_{31}
 R_{31}
 R_{32}
 R_{31}
 R_{32}
 R_{32}
 R_{33}
 R_{31}
 R_{32}
 R_{32}
 R_{33}
 R_{33}
 R_{32}
 R_{33}
 R

and R_{11} , R_{12} , R_{13} , R_{24} , R_{25} , R_{26} , R_{31} , R_{32} , X_4 , X_9 , X_{10} and X_{15} are as defined for formula I. Preferred compounds of formula I are those wherein W is a group

$$R_{16}$$
 R_{15} R_{18} R_{18} R_{20} R_{23} R_{22} R_{22} R_{23} R_{24} R_{25} R

$$R_{28}$$
 R_{27} R_{27} R_{28} R_{27} R_{28} R_{27} R_{28} R_{27} R_{28} R

 X_8 , X_{11} and X_{12} are as defined for formula I.

Also preferred are compounds of formula I wherein R_1 is hydrogen, fluorine or chlorine; R_2 is chlorine, bromine, cyano or CF_3 ; and X_1 is oxygen.

Of those compounds, special preference is given to those wherein R_1 is fluorine or chlorine; and R_2 is chlorine, bromine or cyano, and of those compounds special importance is attached to those wherein R_1 is fluorine; and R_2 is chlorine.

The process according to the invention for the preparation of compounds of formula I

$$R_2 \longrightarrow N$$
 $X_1 \longrightarrow R_3$
(I)

wherein R_1 , R_2 and W are as defined for formula I; X_1 is O or S; R_3 is C_1 - C_6 alkoxy- C_1 - C_6 -alkyl, C_1 - C_6 alkoxy- C_1 - C_6 alkyl, C_1 - C_6 alkyl, C_3 - C_6 alkenyl, C_3 - C_6 alkynyl, C_2 - C_6 -haloalkyl, C_3 - C_6 haloalkenyl, C_3 - C_6 alkyl, C_3 - C_6 haloalkyl, C_3 - C_6 alkyl,

$$\bigcap_{O} C_{H_2^-} \quad , \quad O \\ C_1^- C_3 alkyl \\ CH_2^- \quad , \quad (C_1^- C_5 hydroxyalkyl) - CH_2^-, \ (B_1^- C_1^- C_5 hydroxyalkyl) - CH_2^- \ or \\ CH_2^- \quad , \quad (C_1^- C_5 hydroxyalkyl) - CH_2^-, \ (C_1^- C_5 hydroxyalkyl) - CH_2^- \ or \\ CH_2^- \quad , \quad (C_1^- C_5 hydroxyalkyl) - CH_2^-, \ (C_1^- C_5 hydroxyalkyl) - CH_2^-, \ (C_1^- C_5 hydroxyalkyl) - CH_2^- \ or \\ CH_2^- \quad , \quad (C_1^- C_5 hydroxyalkyl) - CH_2^-, \ (C_1^- C_5 hydroxyalkyl) - CH_2^-, \ (C_1^- C_5 hydroxyalkyl) - CH_2^-, \ (C_1^- C_5 hydroxyalkyl) - CH_2^- \ or \\ CH_2^- \quad , \quad (C_1^- C_5 hydroxyalkyl) - CH_2^-, \ (C_1^- C_5 hydroxyalkyl) - CH_2^-, \ (C_1^- C_5 hydroxyalkyl) - CH_2^-, \ (C_1^- C_5 hydroxyalkyl) - CH_2^- \ or \\ CH_2^- \quad , \quad (C_1^- C_5 hydroxyalkyl) - CH_2^-, \ (C_1^- C_$$

(B₁-C₁-C₅haloalkyl)-CH₂-; and B₁ is as defined for formula I is carried out analogously to known procedures, for example as described in CH Application No. 695/97 and references given therein, and comprises oxidising a compound of formula III

$$R_2 \longrightarrow N$$
 (III),

for example with hydrogen peroxide/urea adduct in the presence of a carboxylic acid and/or a carboxylic acid anhydride, organic peracid or persulfonic acid (Caro's acid) in a suitable solvent, to form a compound of formula V

$$R_{2} = \bigvee_{N^{+}}^{R_{1}} W \qquad (V)$$

and then rearranging that compound in an inert solvent in the presence of an anhydride or in the presence of antimony pentachloride (Katada reaction) to yield, after aqueous working-up and purification, a compound of formula II

$$R_2$$
 N
 N
 $(II),$

the radicals R_1 , R_2 and W in the compounds of formulae II, III and V being as defined, and then alkylating that compound in the presence of an inert solvent and a base with a compound of formula VI

$$R_3$$
-L (VI),

wherein R₃ is as defined and L is a leaving group, preferably chlorine, bromine, iodine,

compounds of formulae I and IV

wherein R_1 , R_2 , R_3 and W are as defined and X_1 is O, and then, after the compound of formula I has been separated from the pyridol derivative of formula IV, optionally functionalising the pyridono derivative of formula I further in accordance with the definition of X_1 and R_3 , for example with the aid of a suitable sulfur reagent to form the corresponding pyridinethione derivative $(X_1 = S)$.

When R_3 in the pyridol derivative of formula IV is an allyl group or a homolog thereof ($R_3 = C_3$ - C_6 allyl group), those pyridol derivatives of formula IVb in Reaction Scheme 1 may be rearranged in a manner analogous to that described, for example, in J. Org. Chem. 50, 764 (1985) and Tetrahedron Lett. 1979, 3949, in the presence of a suitable catalyst, for example palladium(II) chloride/diacetonitrile or palladium(II) chloride/phenylacetonitrile complex, to form the isomeric N-allylated pyridone derivative of formula I ($R_3 = C_3$ - C_6 allyl group). That rearrangement reaction is illustrated in Reaction Scheme 1 below.

Reaction Scheme 1:

The compounds of formula I wherein R_1 , R_2 and W are as defined for formula I, X_1 is oxygen and R_3 is C_1 - C_6 alkyl, C_3 - C_6 alkenyl, C_3 - C_6 alkynyl, C_2 - C_6 haloalkyl or C_3 - C_6 haloalkenyl may be obtained in a manner analogous to that described in J. Org. Chem. 38, 3268 (1973), ibid 16, 1143 (1951), Chem. Communic. 1979, 552 or J. Am. Chem. Soc. 78, 416 (1956) from the compounds of formula IVa

$$\begin{array}{c}
R_{2} \\
\longrightarrow \\
N
\end{array}$$
(IVa),

wherein R₁, R₂ and W are as defined for formula I and R₀₃ is a lower alkoxy group, e.g. C₁-or C₂-alkoxy, benzyloxy or halogen, e.g. chlorine or bromine, by first reacting a compound of formula IVa with an alkylating agent of formula VI

$$R_3$$
-L (VI),

wherein R_3 is C_1 - C_6 alkyl, C_3 - C_6 alkenyl, C_3 - C_6 alkynyl, C_2 - C_6 haloalkyl or C_3 - C_6 haloalkenyl and L is a leaving group, and then either heating or treating with dimethyl sulfoxide, if appropriate in the presence of an alkali metal halide, or with iodine or hydrochloric acid.

The compounds of formula I wherein R_1 , R_2 and W are as defined for formula I, X_1 is oxygen and R_3 is C_1 - C_6 alkyl, C_3 - C_6 alkenyl, C_3 - C_6 alkynyl, C_2 - C_6 haloalkyl, C_3 - C_6 haloalkenyl or C_3 - C_6 cycloalkyl may, in a further synthesis variant, be obtained in a manner analogous to that described in Heterocycles 45, 1059 (1997) or Chem. Pharm. Bull. 2, 193 (1954) from the compounds of formula III

$$R_2 \longrightarrow R_1$$
 (III),

wherein R₁, R₂ and W are as defined, by reaction with an alkylating reagent of formula VI

$$R_3$$
-L (VI),

wherein R_3 is C_1 - C_6 alkyl, C_3 - C_6 alkenyl, C_3 - C_6 alkynyl, C_2 - C_6 haloalkyl, C_3 - C_6 haloalkenyl or C_3 - C_6 cycloalkyl and L is a leaving group, and with an oxidising agent, for example manganese dioxide (MnO₂) or potassium hexacyanoferrate (K_3 Fe(CN)₆).

The process according to the invention for the preparation of compounds of formula I

wherein R_1 , R_2 and W are as defined for formula I; X_1 is S; R_3 is hydroxy, C_1 - C_6 alkoxy, C_3 - C_6 alkenyloxy, C_3 - C_6 alkynyloxy, C_1 - C_6 haloalkoxy, C_3 - C_6 haloalkenyloxy, R_1 - R_1 - R_2 - R_3 - R_4 - R_4 - R_5

$$R_2 \longrightarrow N$$
 (III)

to yield a compound of formula V

$$R_2$$
 N_2^+
 N_2^+
 N_2^+
 N_2^+
 $N_2^ N_2^+$
 $N_2^ N_2^+$
 N_2^-

chlorinating or brominating that compound, for example with phosphorus oxychloride, phosphorus oxybromide, sulfuryl chloride, thionyl chloride or phosphorus pentachloride in phosphorus oxychloride, and then oxidising it again to form a compound of formula VIII

$$R_2$$
 N_2
 N_1
 N_2
 N_2
 N_3
 N_4
 N_3
 N_4
 N_4

the radicals R_1 , R_2 and W in the compounds of formulae III, V and VIII being as defined and Hal in the compound of formula VIII being chlorine or bromine, then converting that compound in the presence of a solvent, e.g. water, an alcohol or a mixture thereof, or an amide, using a suitable sulfur reagent, e.g. hydrogen sulfide, thiourea, sodium hydrogen sulfide (NaSH) or phosphorus pentasulfide (P_2S_5), into a compound of formula Im

and reacting that compound in the presence of a solvent and a base with a compound of formula XI

$$R_{42}$$
-L (XI),

wherein R_{42} is C_1 - C_6 alkyl, C_3 - C_6 alkenyl, C_3 - C_6 alkynyl, C_1 - C_6 haloalkyl, C_3 - C_6 haloalkenyl, C_1 - C_6 alkyl, C_1 - C_6 alkylcarbonyl, C_3 - C_8 trialkylsilyl, hydroxy- C_1 - C_5 alkyl or B_1 - C_1 - C_5 hydroxy-alkyl; B_1 is as defined; and L is a leaving group, e.g. halogen, for example chlorine, bromine

or iodine,
$$CH_3SO_2O$$
-, CH_3 SO_2O - or C_1 - C_6 alkylcarbonyloxy.

The process according to the invention for the preparation of compounds of formula!

$$R_2 \longrightarrow N$$
 N_3
(I)

wherein R_1 , R_2 , R_3 and W are as defined for formula I and X_1 is S is carried out analogously to known procedures, for example as described in WO 98/42698 and references given therein, and comprises treating a compound of formula I

wherein R_1 , R_2 , R_3 and W are as defined and X_1 is O in an inert solvent with a sulfur reagent, for example phosphorus pentasulfide or Lawesson reagent.

For the preparation of the pyridine intermediates of formula III, a large number of known standard procedures of heterocyclic chemistry are available, the choice of a suitable preparation procedure being governed by the properties (reactivities) of the substituents in the respective intermediates.

The process according to the invention for the preparation of compounds of formula III is carried out analogously to known procedures, for example as described in EP-A-0 438 209 or DE-OS 19 604 229, and, for the purpose of preparing compounds of formula III

$$R_2 \longrightarrow N$$
 (III)

wherein R_1 and R_2 are as defined for formula I, W is a group W_1 \longrightarrow N X_2 R_8 (W_1) and

 R_8 , R_9 , R_{10} , X_2 and X_3 are as defined for formula I (corresponding to the compound of formula IIIa in Reaction Scheme 2), comprises, for example, converting a compound of formula XII

wherein R₁ and R₂ are as defined and Hal is fluorine, chlorine or bromine, in the presence of an inert solvent and ammonia, if appropriate in an autoclave at temperatures of from -10 to 180°C, into a compound of formula XIII

$$R_2$$
 NH_2
 NH_2
 NH_2

converting that compound in the presence of a base and a solvent a) with a chloroformic acid ester of formula XIV

$$C_1$$
- C_4 alkylO——C—CI (XIV),

wherein X2 is as defined for formula I, into a compound of formula XV

b) with oxalyl chloride, phosgene or thiophosgene into a compound of formula XVI

$$R_{2} \xrightarrow{R_{1}} N = C = X_{2}$$
 (XVI),

then cyclising the compound of formula XV or XVI in the presence of from 0.1 to 1.5 equivalents of a base in an inert solvent with an enamine derivative of formula XVII

wherein R_9 and R_{10} are as defined for formula I and X_3 is oxygen, to yield a compound of formula XVIII

$$R_{2} \xrightarrow{R_{1}} \underset{X_{3}}{\overset{X_{3}}{\bigvee}} R_{10}$$

$$X_{3} \xrightarrow{R_{10}} R_{9}$$

$$X_{3} \xrightarrow{R_{10}} R_{10}$$

$$X_{4} \xrightarrow{R_{10}} R_{10}$$

$$X_{5} \xrightarrow{R_{10}} R_{10}$$

wherein R_1 , R_2 , R_9 , R_{10} , X_2 and X_3 are as defined, and reacting that compound further in the presence of an inert solvent and a base

c) with a compound of formula XIX

$$R_8$$
-L (XIX),

wherein R₈ is C₁-C₃alkyl or C₁-C₃haloalkyl and L is a leaving group, or

d) with a hydroxylamine derivative of formula XX

$$NH_2-L_1$$
 (XX),

wherein L₁ is a leaving group.

The process according to the invention for the preparation of compounds of formula III is carried out analogously to known procedures, for example as described in DE-A-4 423 934 and JP-A-58 213776, and, for the preparation of compounds of formula III

$$R_2$$
 W (III)

wherein
$$R_1$$
 and R_2 are as defined for formula I, W is a group W_2 N_1 R_{12} R_{12} R_{13}

and R_{11} , R_{12} , R_{13} and X_4 are as defined for formula I (corresponding to the compound of formula IIIb in Reaction Scheme 3), comprises, for example, either

a) converting a compound of formula XII

wherein R_1 and R_2 are as defined and Hal is fluorine, chlorine or bromine, with hydrazine, preferably in a protic solvent, into a compound of formula XXI

$$R_{2} \xrightarrow{R_{1}} NH-NH_{2}$$
 (XXI),

and reacting that compound further with a compound of formula XXII or XXIIa

wherein R_{11} and R_{12} are as defined for formula I, and Hal in the compound of formula XXIIa is chlorine or bromine, or

b) first diazotising a compound of formula XIII

$$R_2$$
 NH_2
 NH_2
 NH_2

wherein R₁ and R₂ are as defined, and then reacting further with a compound of formula XXIII

COOH
$$R_{11}
C
R_{12}
(XXIII),$$

wherein R₁₁ and R₁₂ are as defined, to yield a compound of formula XXIV

$$R_{2} \xrightarrow{R_{1}} H \xrightarrow{O} R_{12} \qquad (XXIV),$$

which is optionally cyclised in the presence of a base, e.g. 4-dimethylaminopyridine, and a compound of formula XXV

$$\begin{array}{c} X_4 & P(phenyl)_3 \\ \parallel & \parallel \\ C_1\text{-}C_4 alkyl\text{-}O\text{-}C\text{-}C\text{-}R_{13} \end{array} \tag{XXV},$$

wherein R₁₃ is as defined and X₄ is oxygen.

The process according to the invention for the preparation of compounds of formula III is carried out analogously to known procedures, for example as described in EP-A-0 272 594, EP-A-0 493 323, DE-A-3 643 748, WO 95/23509, US-A-5 665 681 and US-A-5 661 109, and, for the preparation of compounds of formula III

$$R_2 \longrightarrow R_1$$
 (III)

wherein R_1 and R_2 are as defined for formula I, W is a group W_7 N_7 N_7 R_{26} R_{26} R_{26}

 R_{24} , R_{25} , R_{26} , X_9 and X_{10} are as defined for formula I (corresponding to the compound of formula IIIg in Reaction Scheme 4), comprises, for example, reacting either a) a compound of formula XVa

$$R_{2} \xrightarrow{R_{1}} X_{10}$$

$$|| X_{10}$$

$$|| C - OC_{1} - C_{4} alkyl$$

$$|| X - Va|$$

in the presence of a solvent and a base, or

b) a compound of formula XVIa

$$R_{2} \xrightarrow{R_{1}} N=C=X_{10}$$
 (XVIa),

if appropriate in a suitable solvent, the radicals R_1 , R_2 and X_{10} in the compounds of formulae XVa and XVIa being as defined.

with a compound of formula XXVI

$$\begin{array}{c} R \times X_9 \\ | 1^{25} | | \\ R_{26}NH - C - C - OC_1 - C_4 alky| \\ R_{24} \end{array}$$
 (XXVI),

wherein R_{24} , R_{25} , R_{26} and X_9 are as defined, to yield a compound of formula XXVII

cyclising that compound in the presence of a suitable solvent and a base and then optionally

c) when R₂₆ is hydrogen, reacting with a compound of formula XXVIII

wherein R₂₆ is C₁-C₃alkyl and L is a leaving group.

The process according to the invention for the preparation of compounds of formula III is carried out analogously to known procedures, for example as described in EP-A-0 210 137, DE-A-2 526 358, EP-A-0 075 267 and EP-A-0 370 955, and, for the preparation of compounds of formula III

$$R_2$$
 W (III)

 R_{27} , R_{28} , X_{11} and X_{12} are as defined for formula I (corresponding to the compound of formula IIIh in Reaction Scheme 5), comprises, for example, reacting a) a compound of formula XVb

$$R_{2} \xrightarrow{R_{1}} X_{12}$$

$$\parallel$$

$$NH-C-OC_{1}-C_{4}alkyl$$
(XVb)

in the presence of a solvent and a base, or

b) a compound of formula XVIb

$$R_{2} \xrightarrow{R_{1}} N = C = X_{12}$$
 (XVIb),

the radicals R_1 , R_2 and X_{12} in the compounds of formulae XVb and XVIb being as defined, if appropriate in a suitable solvent,

with a compound of formula XXIX

$$\begin{array}{c} X_{11} \\ \parallel \\ R_{28}NH-N-C-OC_1-C_4alkyl \\ R_{27} \end{array} \tag{XXIX},$$

wherein R₂₇, R₂₈ and X₁₁ are as defined, to yield a compound of formula XXX

cyclising that compound in the presence of a suitable solvent and a base, and then optionally

c) when R_{27} and/or R_{28} are hydrogen, reacting further with a compound of formula XXXIa or XXXIb

$$R_{27}$$
-L (XXXIa) or R_{28} -L (XXXIb),

wherein R_{27} and R_{28} are each independently of the other C_1 - C_3 alkyl and L is a leaving group, or with a Michael acceptor.

The process according to the invention for the preparation of compounds of formula III is carried out analogously to known procedures, for example as described in WO 97/07114, US-A-5 306 694, DE-A-3 832 348, EP-A-0 257 479 and EP-A-0 500 209, and, for the preparation of compounds of formula III

$$R_2$$
 W (III)

wherein R_1 and R_2 are as defined for formula I, W is a group W_3

$$-N$$
 R_{16}
 R_{16}
 R_{16}
 R_{16}

R₁₄, R₁₅ and R₁₆ are as defined for formula I (corresponding to the compound of formula IIIc in Reaction Scheme 6), comprises, for example, condensing a compound of formula XXI

wherein R₁ and R₂ are as defined,

a) with a compound of formula XXXII

$$\begin{array}{cccc}
O & O \\
II & C \\
C & C \\
R_{14} & CH \\
R_{15}
\end{array}$$
(XXXII),

wherein R_{14} is hydrogen, C_1 - C_3 alkyl or C_1 - C_3 haloalkyl; R_{15} is hydrogen, C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_2 - C_4 alkenyl, C_3 - C_5 haloalkenyl or C_3 - or C_4 -alkynyl and R_{16} is hydrogen, C_1 - C_4 alkyl or C_1 - C_4 haloalkyl, if appropriate in the presence of an acidic, basic or bifunctional catalyst, e.g. p-toluenesulfonic acid, or

b) with a compound of formula XXXIIa

wherein R_{15} and R_{16} are as defined and L_2 is a suitable leaving group, to form a compound of formula XXXIII

$$R_{2} \xrightarrow{N_{1}} N \xrightarrow{R_{16}} R_{16}$$
 (XXXIII),

and functionalising the pyrazolone group further in accordance with the definition of R₁₄ analogously to known procedures, for example using a halogenating agent, e.g. phosphorus oxychloride, to form the corresponding halogen derivative of formula IIIc

$$R_{2} = N$$

$$R_{16}$$

$$R_{15}$$
(IIIc),

wherein R₁, R₂, R₁₅ and R₁₆ are as defined and R₁₄ is halogen (Reaction Scheme 6).

The process according to the invention for the preparation of compounds of formula III is carried out analogously to known procedures, for example as described in EP-A-0 370 332, EP-A-0 370 955 or DE-A-3 917 469, and, for the preparation of compounds of formula III

$$R_2$$
 W (III)

wherein R_1 and R_2 are as defined for formula I, W is a group W_4 = R_{18} R_{19}

 (W_4) and R_{17} , R_{18} and R_{19} are as defined for formula I (corresponding to the compound of formula IIId in Reaction Scheme 7), comprises, for example, condensing a compound of formula XXI

wherein R₁ and R₂ are as defined, a) with a compound of formula XXXIIb

$$R_{\overline{18}} = R_{\overline{17}} \qquad (XXXIIb),$$

wherein R₁₈ and R₁₉ are as defined and R₁₇ is hydrogen, C₁-C₄alkyl or C₁-C₄haloalkyl, if appropriate in the presence of a catalyst, or b) with a compound of formula XXXIIc

wherein R_{18} and R_{19} are as defined and L_2 is a suitable leaving group, to form a compound of formula XXXIIIa

$$R_{2} \xrightarrow{R_{1}} N \xrightarrow{R_{18}} R_{19}$$
 (XXXIIIa)

and treating that compound with a halogenating agent, e.g. a phosphorus oxyhalide or thionyl halide, to yield a compound of formula IIId

$$R_{2} \xrightarrow{R_{1}} N \xrightarrow{R_{18}} R_{19}$$
 (IIId),

wherein R_1 , R_2 , R_{18} and R_{19} are as defined and R_{17} is halogen, and optionally reacting that compound with a cyanide of formula XXXIV

$$M(CN)_s$$
 (XXXIV),

wherein M is an ammonium cation, an alkali metal ion or a metal ion from sub-group I or II of the Periodic Table of the Elements and s is the number 1 or 2, if appropriate in the presence of an alkali metal iodide (R_{17} = cyano) (Reaction Scheme 7).

The process according to the invention for the preparation of compounds of formula III is carried out analogously to known procedures, for example as described in DE-A-3 917 469, WO 92/00976, US-A-5 069 711 and EP-A-0 260 228, and, for the preparation of compounds of formula III

$$R_2$$
 W (III)

wherein R_1 and R_2 are as defined for formula I, W is a group W_5 N_5 N_5

$$W_6$$
 R_{22} R_{23} R_{24} R_{25} R_{2

formula I (corresponding to the compounds of formulae IIIe and IIIf, respectively, in Reaction Scheme 8), comprises, for example, reacting

a) a compound of formula XXXV

b) a compound of formula XXXVa

the radicals R_{20} to R_{23} in the compounds of formulae XXXV and XXXVa being as defined, with a compound of formula XIII

$$R_2$$
 NH_2 (XIII),

wherein R₁ and R₂ are as defined, in an inert solvent in the presence of a C₁-C₄alkyl-carboxylic acid at temperatures of from 20° to 200°C, and optionally converting the resulting compound of formula IIIe or IIIf

$$R_{2} \xrightarrow{R_{1}} N_{5} \xrightarrow{R_{20}} R_{20} \text{ (IIIe) or } R_{2} \xrightarrow{R_{1}} X_{8} \xrightarrow{R_{22}} R_{23} \text{ (IIIf),}$$

wherein R_1 , R_2 and R_{20} to R_{23} are as defined and X_5 to X_8 are oxygen, with the aid of a suitable sulfur reagent, into the corresponding thiono compound of formula IIIe or IIIf wherein X_5 and/or X_6 and X_7 and/or X_8 are sulfur respectively (Reaction Scheme 8).

The process according to the invention for the preparation of compounds of formula III is carried out analogously to known procedures, for example as described in WO 95/00521, EP-A-0 611 708 and WO 94/25467, and, for the preparation of compounds of formula III

$$R_2$$
 W (III)

wherein R_1 and R_2 are as defined for formula I, W is a group W_9 X_{14} X_{15} X_{15}

 R_{29} , R_{30} , X_{13} and X_{14} are as defined for formula I (corresponding to the compound of formula IIIi in Reaction Scheme 9), comprises, for example, reacting a) a compound of formula XVc

$$R_{2} \xrightarrow{R_{1}} NH - C - OC_{1} - C_{4}alkyl$$
 (XVc) or

b) a compound of formula XVic

$$R_{2} \xrightarrow{R_{1}} N = C = X_{14}$$
 (XVIc),

the radicals R_1 , R_2 and X_{14} in the compounds of formula XVc and XVIc being as defined, if appropriate in the presence of a solvent and a base, with a compound of formula XXXVI R_{30} -NH-NH- R_{29} (XXXVI),

wherein R₂₉ and R₃₀ are as defined for formula I, to yield a compound of formula XXXVII

$$R_{2} = NH - C - N - NH - R_{29}$$

$$R_{30} = N + R_{30}$$
(XXXVII),

and then reacting that compound, if appropriate in a solvent and in the presence of a base, with a (thio)carbonylating reagent of formula XXXVIII

$$\begin{array}{c}
L_3 \\
C = X_{13}
\end{array}$$
(XXXVIII),

wherein X₁₃ is as defined and L₃ is a leaving group (Reaction Scheme 9).

The process according to the invention for the preparation of compounds of formula III is carried out analogously to known procedures, for example as described in US-A-5 980 480, DE-A-3 917 469, US-A-4 818 275, US-A-5 041 155 and EP-A-0 610 733, and, for the preparation of compounds of formula III

$$R_2$$
 W (III)

wherein
$$R_1$$
 and R_2 are as defined for formula I, W is a group W_{10} N R_{32} N R_{32}

and R_{31} , R_{32} and X_{15} are as defined for formula I (corresponding to the compound of formula IIIk in Reaction Scheme 10), comprises, for example,

a) reacting a compound of formula XXI

if appropriate in the presence of a catalyst, with a compound of formula XXXIX

$$R_{32}$$
 $C=0$ (XXXIX)

to form a compound of formula XXXX

$$R_{2} \xrightarrow{R_{1}} NHN = C \xrightarrow{R_{32}} (XXXX)$$

the radicals R_1 , R_2 and R_{32} in the compounds of formulae XXI, XXXIX and XXXX being as defined, and cyclising the compound of formula XXXX by further reaction with an azide of formula XXXXI

$$\begin{array}{c}
O\\II\\N_3 \longrightarrow P(OC_1 - C_4 alkyl)_2
\end{array} (XXXXI)$$

 $(X_{15} = O, R_{31} = H)$, or

b) cyclising a compound of formula XXI

$$R_{2} \xrightarrow{R_{1}} NHNH_{2}$$
 (XXI)

with a compound of formula XXXXIII

$$\begin{array}{c} \text{OC}_1\text{-C}_4\text{alkyl} \\ \text{I} \\ \text{C} \\ \text{N-COOC}_1\text{-C}_4\text{alkyl} \end{array} \tag{XXXXIII),}$$

the radicals R_1 , R_2 and R_{32} in the compounds of formulae XXI and XXXXIII being as defined, $(X_{15}=O,\,R_{31}=H)$, or

c) reacting a compound of formula XXI

first with a compound of formula XXXXIV

to form a compound of formula XXXXa

$$R_2$$
 $NH-N=CH-R_{32}$
 $(XXXXa),$

and then with an alkali metal cyanate to form a compound of formula XXXXV

$$R_{2} \xrightarrow{N-N=CH-R_{32}} N \xrightarrow{N-N=CH-R_{32}} (XXXXV)$$

and finally cyclising that compound in the presence of an oxidising agent, to yield a compound of formula IIIk

$$R_{2} = N_{N} = N_{N} = N_{32}$$
 (IIIk),

wherein R_{1} , R_{2} and R_{32} are as defined, X_{15} is oxygen and R_{31} is hydrogen, and optionally treating that compound with a sulfur reagent ($X_{15} = S$) and, in the presence of a base, with an alkylating reagent of formula XXXXII

wherein R_{31} is C_1 - C_4 alkyl, C_1 - C_4 haloalkyl, C_3 - or C_4 -alkenyl, C_3 - or C_4 -haloalkenyl or C_3 - or C_4 -alkynyl and L is a leaving group.

The preparation of the compounds of formula IIIa

$$R_{2} \xrightarrow{R_{1}} X_{3} \xrightarrow{R_{10}} R_{9}$$
 (IIIa)

wherein R_1 , R_2 , R_8 , R_9 , R_{10} , X_2 and X_3 are as defined for formula I is illustrated in Reaction Scheme 2 below.

Reaction Scheme 2:

For the preparation of the compounds of formula IIIa according to the invention, a large number of known standard procedures are available, for example as described in EP-A-0 438 209 and DE-OS-19 604 229 (R_9 =cyano). Reaction Scheme 2 shows a selection of suitable preparation procedures, the choice of the reaction routes and the reagents being governed by the reactivities of the substituents in the intermediates.

Starting, for example, from a compound of formula XII, it is possible by reaction with ammonia in an inert solvent, if appropriate in an autoclave at temperatures of from -10 to 180°C, to obtain an aminopyridine of formula XIII. The latter compound may be converted in the presence of a base and a solvent either

- a) with a chloroformic acid ester of formula XIV ($X_2 = O$ or S) into a pyridyl carbamate of formula XV, or
- b) with oxalyl chloride, phosgene (X₂ =O) or thiophosgene (X₂ =S) into an iso(thio)cyanate of formula XVI. Such reactions are described, for example, in Angew. 1971, 407.

The carbamate and the iso(thio)cyanate of formulae XV and XVI may be cyclised in the presence of an enamine derivative of formula XVII in an inert solvent to form a uracil derivative of formula XVIII, the reaction of the iso(thio)cyanate of formula XVI advantageously being carried out in the presence of from 0.1 to 1.5 equivalents of a base, e.g. sodium hydride, potassium tert-butanolate or an alkaline earth metal oxide or hydroxide, e.g. barium hydroxide.

The desired compounds of formula IIIa may be prepared in accordance with standard procedures from the uracils of formula XVIII in the presence of an inert solvent and at least one equivalent of a base, for example an alkali metal carbonate, such as potassium carbonate,

- c) with an alkylating agent of formula XIX to form the N-alkyl derivative of formula IIIa (R₈ =alkyl), or
- d) analogously to WO 97/05116 with a hydroxylamine derivative of formula XX, wherein L₁

is a leaving group, e.g.
$$HOS(O)_2O$$
-, NO_2 or H_3C $OS(O)_2$ -, CH_3

for example 2,4-dinitrophenyl-hydroxylamine or hydroxylamine-O-sulfonic acid, to form the N-amino derivative of formula IIIa (R_8 =amino). The desired thiono derivatives of formula IIIa (X_2 , X_3 =S) may be obtained by thionation, for example with phosphorus pentasulfide or Lawesson reagent.

The preparation of the compounds of formula IIIb

$$R_{2} \xrightarrow{R_{1}} X_{4} \xrightarrow{R_{13}} R_{12}$$

$$R_{11} \xrightarrow{R_{11}} R_{12}$$

$$R_{11} \xrightarrow{R_{12}} R_{12}$$

$$R_{11} \xrightarrow{R_{12}} R_{12}$$

$$R_{11} \xrightarrow{R_{12}} R_{12}$$

wherein R_1 , R_2 , R_{11} , R_{12} , R_{13} and X_4 are as defined for formula I, is illustrated in Reaction Scheme 3 below.

Reaction Scheme 3:

The compounds of formula IIIb may be prepared in accordance with known methods, for example in accordance with Reaction Scheme 3 (variant a)), by reacting a 2-halopyridine

derivative of formula XII with hydrazine, preferably in a protic solvent, e.g. an alcohol, analogously to GB-A-2 230 261 to form a 2-hydrazino derivative of formula XXI. The latter is reacted with a diketone of formula XXII analogously to DE-OS-19 754 348 or with a dihaloketone of formula XXIIa analogously to WO 97/07104 to form a hydrazone derivative of formula XXIV.

The subsequent cyclisation to form the desired compound of formula IIIb is carried out in the presence of a phosphorane derivative of formula XXV if appropriate in the presence of a base, for example 4-dimethylaminopyridine. Then, for the case where X_4 in a compound of formula IIIb = O, thionation (X_4 = S) may be carried out in a manner analogous to that described under Reaction Scheme 2.

According to Reaction Scheme 3, the hydrazone derivative of formula XXIV may also be obtained from the 2-aminopyridine derivative of formula XIII *via* diazotisation, preferably with exclusion of water, and subsequent coupling to the ketonic acid of formula XXIII (Japp-Klingemann reaction analogously to DE-OS-19 754 348) (variant b) in Reaction Scheme 3).

The preparation of the compounds of formula IIIg

wherein R_1 , R_2 , R_{24} , R_{25} , R_{26} , X_9 and X_{10} are as defined for formula I, is illustrated in Reaction Scheme 4 below.

Reaction Scheme 4:

a)
$$R_2$$
 X_{10}
 X

The compounds of formula IIIg may be prepared analogously to known methods, for example as described in EP-A-0 272 594, EP-A-0 493 323, DE-A-3 643 748, WO 95/23509, US-A-5 665 681 or US-A-5 661 109.

For example, in accordance with Reaction Scheme 4 either

a) a carbamate derivative of formula XVa may be cyclised in the presence of a solvent and a base, or

b) an iso(thio)cyanate of formula XVIa may be cyclised, if appropriate in a suitable solvent, with an amino acid derivative of formula XXVI via a compound of formula XXVII in the presence of a base and a suitable solvent to form a compound of formula IIIg. For the case where in a compound of formula IIIg R_{26} is hydrogen and X_9 and/or X_{10} are oxygen, then optionally alkylation may be carried out at the free N atom of the hydantoin ring using an alkylating reagent of formula XXVIII and the ring carbonyl group may be thionated (X_9 and/or $X_{10} = S$).

The preparation of compounds of formula IIIh

wherein R_1 , R_2 , R_{27} , R_{28} , X_{11} and X_{12} are as defined for formula I, is illustrated in Reaction Scheme 5 below.

Reaction Scheme 5:

a)
$$R_2$$
 X_{12}
 X_{12}
 X_{12}
 X_{13}
 X_{14}
 X_{15}
 X

The compounds of formula IIIh may be prepared analogously to known procedures, for example as described in EP-A-0 210 137, DE-OS-2 526 358, EP-A-0 075 267 or EP-A-0 370 955.

For example, in accordance with Reaction Scheme 5 either

- a) a carbamate derivative of formula XVb may be cyclised in the presence of a solvent and a base, or
- b) an iso(thio)cyanate of formula XVIb may be cyclised, if appropriate in a suitable solvent, with a carbazate of formula XXIX *via* a compound of formula XXX in the presence of a base and a suitable solvent to form a compound of formula IIIh.

For the case where in a compound of formula IIIh R_{27} and/or R_{28} are hydrogen and X_{11} and/or X_{12} are oxygen, then alkylation may be carried out at the free N atoms using an alkylating agent of formula XXXIa or XXXIb and the ring carbonyl groups may be thionated $(X_{11} \text{ and/or } X_{12} = S)$ using a thionating reagent.

For the preparation of compounds of formula IIIh in Reaction Scheme 5 wherein R_{27} and R_{28} together form an alkylene bridge that is interrupted e.g. by $-S(O)_2$ -, for example a compound of formula IIIh wherein R_{27} and R_{28} are hydrogen may be reacted with a corresponding Michael acceptor, for example CH_2 =CH- $S(O)_2$ CH $_3$ or CH_2 =CH- $S(O)_2$ -CH= CH_2 , and the resulting Michael addition products may be functionalised further.

The preparation of the compounds of formula IIIc

$$R_{2} \xrightarrow{R_{1}} N \xrightarrow{R_{16}} R_{16}$$

$$R_{14} \xrightarrow{R_{15}} R_{15}$$
(IIIc),

wherein R_1 , R_2 and R_{14} to R_{16} are as defined for formula I, is illustrated in Reaction Scheme 6 below.

Reaction Scheme 6:

$$R_{2} \xrightarrow{R_{1}} NHNH_{2}$$

$$XXI$$

$$XXI$$

$$A = \frac{R_{1}}{R_{15}}$$

$$XXII$$

$$A = \frac{R_{1}}{R_{15}}$$

$$XXIII$$

$$A = \frac{R_{1}}{R_{15}}$$

$$A = \frac{R_{1}}{$$

In accordance with Reaction Scheme 6, the pyrazole compounds of formula IIIc may be prepared, for example, either from the hydrazinopyridine derivatives of formula XXII by means of condensation with a 1,3-dicarbonyl derivative of formula XXXII (variant a)), or by means of condensation with a β -carbonylcarboxylic acid derivative of formula XXXIIa wherein L_2 is a leaving group, for example C_1 - C_4 alkoxy, hydroxy or halogen, e.g. chlorine or bromine, (variant b)) and subsequent treatment of the resulting pyridylpyrazolone derivative of formula XXXIII with a halogenating agent, for example phosphorus oxychloride (R_{14} =halogen). The two reaction steps a) and b) in Reaction Scheme 6 are effected, if appropriate, in the presence of an acidic, basic or bifunctional catalyst, e.g. p-toluenesulfonic acid.

The compounds of formula IIIc obtained in this way may be functionalised further in accordance with the definitions of the substituents R_{14} to R_{16} by means of standard procedures.

The compounds of formula IIIc in Reaction Scheme 6 wherein R₁₅ is hydrogen may be functionalised further in accordance with the definition of R₁₅, for example with an electrophilic reagent, e.g. a halogenating agent, such as elemental halogen or sulfuryl

halide, to form the corresponding compounds of formula IIIc wherein R_{15} is halogen, or with a nitrating agent, such as nitric acid, if appropriate in admixture with a further strong acid, such as sulfuric acid, to form the corresponding compounds of formula IIIc wherein R_{15} is nitro.

The corresponding pyridono derivatives of formula Ic

$$R_2$$
 N
 R_{16}
 R_{16}
 R_{16}
 R_{15}
(Ic),

wherein R_1 to R_3 , R_{14} to R_{16} and X_1 are as defined for formula I, may be obtained, as described above, from compounds of formula IIIc by means of oxidation of the pyridyl moiety.

In a further variant, the pyridono derivatives of formula Ic may also be obtained directly from the corresponding pyridonylhydrazines of formula XXIa

wherein R_1 to R_3 and X_1 are as defined, analogously to the variants shown in Reaction Scheme 6.

The required pyridonylhydrazine of formula XXIa may readily be obtained from the corresponding pyridonyl halide of formula XIIa

$$R_2$$
 Hal $(XIIa),$ R_3

wherein R_1 , R_2 and R_3 are as defined and Hal is fluorine, chlorine or bromine, with hydrazine, preferably in a protic solvent.

In certain cases, the compounds of formula Ic may also be obtained in manner analogous to that described in J. Het. Chem. 15, 1221 (1978) and in Reaction Scheme 11, by substitution of a pyridonyl derivative of formula XIIa that is provided with a leaving group L₄,

e.g. a halide, a C_1 - C_4 alkyl- or phenyl-sulfonyl group or an unsubstituted or substituted C_1 - C_4 alkyl- or phenyl-sulfonyloxy group, (variant c) in Reaction Scheme 11), or by substitution of a pyridine derivative of formula XII that is provided with a leaving group L_4 , e.g. a halide, a C_1 - C_4 alkyl- or phenyl-sulfonyl group or an unsubstituted or substituted C_1 - C_4 alkyl- or phenyl-sulfonyloxy group, (variant d) in Reaction Scheme 11), with a pyrazole of formula W_{03} or an alkali metal salt thereof, and in the case of variant d) by subsequent functionalisation (oxidation) of the pyridyl moiety of the compound of formula IIIc. The substitution reactions according to variants c) and d) may optionally be carried out in the presence of a suitable solvent and a base.

Reaction Scheme 11:

$$R_2$$
 X_1
 R_3
 X_1
 R_3
 R_{14}
 R_{15}
 R_{15}

The preparation of the compounds of formula IIId

$$R_{2} \xrightarrow{R_{1}} N \xrightarrow{R_{18}} R_{18}$$

$$R_{17} \xrightarrow{R_{19}} R_{19}$$
(IIId)

wherein R_1 , R_2 and R_{17} to R_{19} are as defined for formula I is illustrated in Reaction Scheme 7 below.

Reaction Scheme 7:

$$R_{1}$$

$$R_{2}$$

$$R_{2}$$

$$R_{1}$$

$$R_{2}$$

$$R_{2}$$

$$R_{1}$$

$$R_{2}$$

$$R_{2}$$

$$R_{2}$$

$$R_{3}$$

$$R_{1}$$

$$R_{1}$$

$$R_{1}$$

$$R_{1}$$

$$R_{2}$$

$$R_{2}$$

$$R_{3}$$

$$R_{2}$$

$$R_{3}$$

$$R_{4}$$

$$R_{1}$$

$$R_{2}$$

$$R_{3}$$

$$R_{4}$$

$$R_{4}$$

$$R_{5}$$

$$R_{5$$

In accordance with Reaction Scheme 7, the tetrahydroindazole compounds of formula IIId may be obtained according to known procedures from the hydrazinopyridine derivatives of formula XXI, for example either by condensation with a cyclohexanone derivative of formula XXXIIb that is acylated in the 2-position, wherein R₁₇ is as defined for formula I with the exception of R₁₇ as halogen or cyano, (variant a)), or by condensation with a cyclohexanone derivative of formula XXXIIc wherein L₂ is a leaving group, for example C₁-C₄alkoxy, hydroxy or halogen, e.g. chlorine or bromine, and subsequent halogenation (variant b)) in a manner analogous to that described under Reaction Scheme 6.

The halogen derivatives of formula IIId wherein R_{17} is halogen may be converted into the corresponding cyano-substituted derivatives of formula IIId (R_{17} =CN) according to known methods with an alkali metal cyanide, ammonium cyanide or a metal cyanide, the metal being selected from sub-groups I and II of the Periodic Table of the Elements, if appropriate with the addition of an alkali metal iodide.

The preparation of the compounds of formulae IIIe and IIIf

wherein R_1 , R_2 , R_{20} to R_{23} and X_5 to X_8 are as defined for formula I, is illustrated in Reaction Scheme 8 below.

Reaction Scheme 8:

a)
$$R_2$$
 NH_2 $XIII$ $Solvent, propionic acid, R_2 NH_2 $N$$

In accordance with Reaction Scheme 8, the pyrrolinedione derivatives of formula IIIe and the tetrahydroisoindolinedione derivatives of formula IIIf may be obtained analogously to known procedures, for example by reaction of an anhydride of formula XXXV (variant a)) or XXXVa (variant b)) with an aminopyridine of formula XIII in an inert solvent, for example an ether, e.g. dioxane, or a lower alkylcarboxylic acid, e.g. propionic acid, at temperatures of from 20 to 200°C.

The compounds of formulae IIIe and IIIf (X_5 to $X_8 = O$) obtained in accordance with Reaction Scheme 8 may optionally be thionated with a suitable sulfur reagent (X_5 to $X_8 = S$).

The corresponding pyridono derivatives of formulae le and If

may be obtained from the compounds of formulae IIIe and IIIf as described above, by means of oxidation of the pyridyl moiety.

In a further variant, the pyridono derivatives of formulae le and lf may also be obtained directly from the corresponding aminopyridone derivatives of formula XIIIa

$$R_2$$
 NH_2
 NH_3
 NH_3
 NH_3

wherein R_1 , R_2 , R_3 and X_1 are as defined for formula I, analogously to the method as described in Reaction Scheme 8.

The preparation of the compounds of formula IIIi

$$R_{2} \xrightarrow{R_{1}} N = X_{14} \times X_{13} \times X_{13} \times X_{14} \times X_{13} \times X_{14} \times$$

wherein R_1 , R_2 , R_{29} , R_{30} , X_{13} and X_{14} are as defined for formula I is illustrated in Reaction Scheme 9 below.

Reaction Scheme 9:

In accordance with Reaction Scheme 9, the compounds of formula Illi may be prepared according to known procedures, for example by first reacting a carbamate of formula XVc (variant a)) or an isothiocyanate of formula XVIc (variant b)) with a hydrazine derivative of formula XXXVI to form a semicarbazide derivative of formula XXXVII and then reacting the latter in the presence of a carbonylating or thiocarbonylating reagent of formula XXXVIII. Both reaction steps are advantageously carried out in a suitable solvent and in the presence of a base. As (thio)carbonylating reagent of formula XXXVIII there come into consideration e.g. phosgene, diphosgene, thiophosgene and carbonyldiimidazole. L₃ in formula XXXVIII is therefore a leaving group, for example halogen, e.g. chlorine or bromine,

trichloromethoxy or -N

The corresponding pyridono derivatives of formula li

wherein R_1 to R_3 , R_{29} , R_{30} , X_1 , X_{13} and X_{14} are as defined for formula I, may be obtained from the compounds of formula IIIi in the manner described above, by means of oxidation of the pyridyl moiety.

In a further variant, the pyridono derivatives of formula li may also be obtained directly from the corresponding pyridone carbamates of formula XVd

$$R_{2} \xrightarrow{R_{1}} NH - C - OC_{1} - C_{4} alkyl$$
 (XVd)

or from the iso(thio)cyanates of formula XVId

$$R_{2} \xrightarrow{R_{1}} N = C = X_{14}$$
 (XVId),

the radicals R_1 to R_3 , X_1 and X_{14} in the compounds of formulae XVd and XVId being as defined for formula I, in a manner analogous to that described in Reaction Scheme 9. The required starting compounds of formulae XVc and XVIc are known and are described, for example, in EP-A-0 468 924 and EP-A-0 304 920.

The preparation of the compounds of formula IIIk

$$R_{2} \xrightarrow{R_{1}} N \xrightarrow{N} R_{32}$$

$$X_{15} \qquad R_{31}$$
(IIIk),

wherein R_1 , R_2 , R_{31} , R_{32} and X_{15} are as defined for formula I, is illustrated in Reaction Scheme 10 below.

Reaction Scheme 10:

In accordance with Reaction Scheme 10, the triazolone derivatives of formula IIIk may be prepared analogously to known procedures, for example by using as starting material a hydrazinopyridine derivative of formula XXI which, in accordance with variant a), is reacted with a keto acid of formula XXXIX, advantageously in the presence of an acid catalyst, e.g. a lower alkylcarboxylic acid, e.g. propionic acid, a mineral acid, e.g. sulfuric acid or hydrochloric acid, or a sulfonic acid, e.g. p-toluenesulfonic acid, to form a hydrazone derivative of formula XXXX. The latter may then be cyclised with an azide of formula XXXXI to form a triazolone derivative of formula IIIk wherein X₁₅ is oxygen and R₃₁ is hydrogen and then optionally derivatised further in accordance with standard procedures with an alkylating reagent of formula XXXXII or with a sulfur reagent.

In accordance with variant b), a hydrazinopyridine derivative of formula XXI may be cyclised with an imino ether of formula XXXXIII to form a triazolone derivative of formula IIIk wherein X_{15} is oxygen and R_{31} is hydrogen and then optionally alkylated or thionated as described under variant a).

In accordance with variant c), in Reaction Scheme 10 a hydrazinopyridine derivative of formula XXI may be converted first with an aldehyde of formula XXXXIV, then in the presence of a lower alkylcarboxylic acid, e.g. acetic acid, with an alkali metal cyanate to form a compound of formula XXXXV, which may or may not be isolated, and finally cyclised

with an oxidising agent, e.g. an alkali metal hypochlorite (Javelle), to form a compound of formula IIIk wherein X_{15} is oxygen and R_{31} is hydrogen. The resulting compound of formula IIIk may then optionally be alkylated or thionated as described under variant a). The corresponding pyridono derivatives of formula Ik

wherein R_1 to R_3 , R_{31} , R_{32} , X_1 and X_{15} are as defined for formula I, may be obtained from the compounds of formula IIIk as described above, by means of oxidation of the pyridyl moiety.

As a further variant, the pyridono derivatives of formula lk may also be obtained directly from the corresponding pyridonylhydrazines of formula XXIa

$$R_2$$
 $NHNH_2$ (XXIa),

wherein R_1 to R_3 and X_1 are as defined, in a manner analogous to the variants shown in Reaction Scheme 10.

The compounds of formulae XII and XIII are known or may be prepared in accordance with known methods, for example as described in DE-A-3 917 469; WO 97/07114; WO 92/00976; JP-A-58-213 776; EP-A-0 012 117; EP-A-0 306 547; EP-A-0 030 215; EP-A-0 272 824; EP-A-0 500 209; US-A-4 996 323; US-A-5 017 705; WO 97/05112; J. Het. Chem. 11, 889 (1974); J. Het. Chem 21, 97 (1984); Tetrahedron 41, 4057 (1985); Heterocycles 22,117; Synth. 1988, 938; J. Med. Chem. 25, 96.

The 2-aminopyridines of formula XIII may also be prepared by degradation reactions according to Curtius, Hofmann or Lossen from corresponding pyridine derivatives with carboxylic acid, carboxylic acid chloride, carboxylic acid azide, carboxylic acid ester or carboxylic acid amide functions in the 2-position.

The compounds of formulae XII and XIIa in Reaction Scheme 11 wherein L_4 is a leaving group, e.g. a C_1 - C_4 alkyl- or phenyl-sulfonyl group, are known or may be prepared in accordance with known methods, for example by oxidation of the corresponding thioethers

with hydrogen peroxide or Javelle water or by means of the synthesis of the heterocycle. Such syntheses are described, for example, in Synthesis 1989, 623 or in WO 98/11071.

The reagents of formulae XIV, XVa, XVb, XVIa, XVIb, XVII, XIX, XX, XXII, XXIIa, XXIII, XXV, XXVI, XXVIII, XXIX, XXXIIa, XXXIIb, XXXIIb, XXXIIb, XXXIIb, XXXIIb, XXXIIIb, XXXIIIb, XXXIIV, XXXV, XXXVI, XXXVIII, XXXXIII, XXXXIII, XXXXIII and XXXXIV used in Reaction Schemes 2 to 10 are either known or may be prepared in analogy to known methods.

The intermediates of formula II

in which R_1 , R_2 and W are as defined for formula I and which may be in the tautomeric keto-enol form, are novel. The invention therefore relates to those compounds also.

The reactions to form compounds of formula I are advantageously carried out in aprotic, inert organic solvents. Such solvents are hydrocarbons, such as benzene, toluene, xylene or cyclohexane, chlorinated hydrocarbons, such as dichloromethane, trichloromethane. tetrachloromethane or chlorobenzene, ethers, such as diethyl ether, ethylene glycol dimethyl ether, diethylene glycol dimethyl ether, tetrahydrofuran or dioxane, nitriles, such as acetonitrile or propionitrile, amides, such as N,N-dimethylformamide, N,N-diethylformamide or N-methylpyrrolidinone. The reaction temperatures are preferably from -20°C to +120°C. The reactions are generally slightly exothermic and may usually be carried out at room temperature. In order to shorten the reaction time or alternatively to initiate the reaction, the reaction mixture may be heated to its boiling point for a short time. The reaction times may likewise be shortened by the addition of a few drops of base as reaction catalyst. Suitable bases are especially tertiary amines, such as trimethylamine, triethylamine, quinuclidine, 1,4-diazabicyclo[2.2.2]octane, 1,5-diazabicyclo[4.3.0]non-5-ene or 1,5diazabicyclo[5.4.0]undec-7-ene, but it is also possible to use inorganic bases, such as hydrides, e.g. sodium or calcium hydride, hydroxides, such as sodium or potassium hydroxide, carbonates, such as sodium or potassium carbonate, or hydrogen carbonates, such as potassium or sodium hydrogen carbonate.

The compounds of formula I can be isolated in customary manner by concentration and/or evaporation of the solvent and can be purified by recrystallisation or trituration of the solid residue in solvents in which they are not readily soluble, such as ethers, aromatic hydrocarbons or chlorinated hydrocarbons, or by means of column chromatography and a suitable eluant.

For the use according to the invention of the compounds of formula I, or of compositions comprising them, there come into consideration all methods of application customary in agriculture, for example pre-emergence application, post-emergence application and seed dressing, and also various methods and techniques such as, for example, the controlled release of active ingredient. For that purpose a solution of the active ingredient is applied to mineral granule carriers or polymerised granules (urea/formaldehyde) and dried. If required, it is also possible to apply a coating (coated granules), which allows the active ingredient to be released in metered amounts over a specific period of time.

The compounds of formula I may be used as herbicides in their unmodified form, that is to say as obtained in the synthesis, but they are preferably formulated in customary manner together with the adjuvants conventionally employed in formulation technology, for example into emulsifiable concentrates, directly sprayable or dilutable solutions, dilute emulsions, wettable powders, soluble powders, dusts, granules or microcapsules. Such formulations are described, for example, on pages 9 to 13 of WO 97/34485. As with the nature of the compositions, the methods of application, such as spraying, atomising, dusting, wetting, scattering or pouring, are chosen in accordance with the intended objectives and the prevailing circumstances.

The formulations, that is to say the compositions, preparations or mixtures comprising the compound (active ingredient) of formula I or at least one compound of formula I and, usually, one or more solid or liquid formulation adjuvants, are prepared in known manner, e.g. by homogeneously mixing and/or grinding the active ingredients with the formulation adjuvants, for example solvents or solid carriers. Surface-active compounds (surfactants) may also be used in addition in the preparation of the formulations. Examples of solvents and solid carriers are given, for example, on page 6 of WO 97/34485.

Depending on the nature of the compound of formula I to be formulated, suitable surfaceactive compounds are non-ionic, cationic and/or anionic surfactants and surfactant mixtures having good emulsifying, dispersing and wetting properties. Examples of suitable anionic, non-ionic and cationic surfactants are listed, for example, on pages 7 and 8 of

WO 97/34485.

In addition, the surfactants conventionally employed in formulation technology, which are described, *inter alia*, in "McCutcheon's Detergents and Emulsifiers Annual" MC Publishing Corp., Ridgewood New Jersey, 1981, Stache, H., "Tensid-Taschenbuch", Carl Hanser Verlag, Munich/Vienna 1981, and M. and J. Ash, "Encyclopedia of Surfactants", Vol. I-III, Chemical Publishing Co., New York, 1980-81, are also suitable for the preparation of the herbicidal compositions according to the invention.

The herbicidal formulations generally contain from 0.1 to 99 % by weight, especially from 0.1 to 95 % by weight, of herbicide, from 1 to 99.9 % by weight, especially from 5 to 99.8 % by weight, of a solid or liquid formulation adjuvant, and from 0 to 25 % by weight, especially from 0.1 to 25 % by weight, of a surfactant. Whereas commercial products will preferably be formulated as concentrates, the end user will normally employ dilute formulations. The compositions may also comprise further ingredients, such as stabilisers, for example vegetable oils or epoxidised vegetable oils (epoxidised coconut oil, rape oil or soybean oil), antifoams, for example silicone oil, preservatives, viscosity regulators, binders, tackifiers, and also fertilisers or other active ingredients.

The compounds of formula I are generally applied to plants or the locus thereof at rates of application of from 0.001 to 4 kg/ha, especially from 0.005 to 2 kg/ha. The concentration required to achieve the desired effect can be determined by experiment. It is dependent on the nature of the action, the stage of development of the cultivated plant and of the weed and on the application (place, time, method) and may vary within wide limits as a function of those parameters.

The compounds of formula I are distinguished by herbicidal and growth-inhibiting properties, allowing them to be used in crops of useful plants, especially cereals, cotton, soybeans, sugar beet, sugar cane, plantation crops, rape, maize and rice, and also for non-selective weed control. The term "crops" is to be understood as including also crops that have been made tolerant to herbicides or classes of herbicides as a result of conventional methods of breeding or genetic techniques. The weeds to be controlled may be either monocotyledonous or dicotyledonous weeds, such as, for example, Stellaria, Nasturtium, Agrostis, Digitaria, Avena, Setaria, Sinapis, Lolium, Solanum, Echinochloa, Scirpus, Monochoria, Sagittaria, Bromus, Alopecurus, Sorghum halepense, Rottboellia, Cyperus, Abutilon, Sida, Xanthium, Amaranthus, Chenopodium, Ipomoea, Chrysanthemum, Galium, Viola and Veronica.

The following Examples further illustrate but do not limit the invention.

Preparation Examples:

Example P1: Preparation of 2-N-ethoxycarbonylamino-3-fluoro-5-chloro-pyridine

294 g of 2-amino-3-fluoro-5-chloro-pyridine are dissolved in 1 litre of dry pyridine and cooled to 0°C; 220 g of ethyl chloroformate are added dropwise, with stirring, and the mixture is stirred at 22°C until reaction is complete. The reaction mixture is then poured into ice-water, adjusted to pH 4-5 with 2N hydrochloric acid and extracted with ethyl acetate. The combined extracts are washed with water, dried over sodium sulfate, concentrated by evaporation and caused to crystallise by the addition of n-hexane. The resulting precipitate is filtered off, washed with n-hexane and dried *in vacuo*, yielding the desired title compound having a melting point of 132°C.

Example P2: Preparation of 1-(3-fluoro-5-chloro-pyridin-2-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione

Under a nitrogen atmosphere, with cooling and stirring, a solution of 22.7 g of 4,4,4-trifluoro-3-amino-2-butenoic acid ethyl ester is added dropwise at 0-5°C to 5.1 g of a previously prepared sodium hydride dispersion (60%) in 60 ml of N-methylpyrrolidine and the mixture is stirred at 22°C until the evolution of hydrogen has ceased. 23.7 g of 2-ethoxycarbonylamino-3-fluoro-5-chloro-pyridine (Example P1) are then added and the reaction mixture is heated at 120°C for about 5 hours. The mixture is then cooled, 16.7 g of methyl iodide are added dropwise and stirring is carried out at 22°C overnight. The reaction mixture is taken up in ethyl acetate and then washed with ice-water, dried over sodium sulfate, filtered and concentrated by evaporation. The resulting residue is recrystallised from ethyl acetate/n-hexane, yielding the desired title compound having a melting point of 133-134°C.

Example P3: Preparation of 1-(3-fluoro-5-chloro-2-pyridyl-N-oxide)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione

24 g of 1-(3-fluoro-5-chloro-pyridin-2-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione (Example P2) in 150 ml of dichloromethane are cooled to -5°C and 2 g of hydrogen peroxide/urea adduct are added. 2.7 ml of trifluoroacetic acid anhydride dissolved in 2 ml of dichloromethane are then metered in dropwise and after the exothermic reaction has subsided the reaction mixture is stirred overnight to complete the reaction. A further 5 g of hydrogen peroxide/urea adduct and 3 ml of trifluoroacetic acid anhydride are then added in two portions in the course of 3 hours and after the exothermic reaction has subsided the reaction mixture is heated at 25-35°C until the reaction is complete. The reaction mixture is then cooled and at -5°C adjusted to pH 7.5 first with 2N sodium hydroxide solution and then with saturated sodium hydrogen carbonate solution and partitioned between dichloromethane and ice-water; the organic phase is separated off, dried over sodium sulfate, filtered and concentrated by evaporation. The solid residue that remains is recrystallised from ethyl acetate/n-hexane, yielding the desired product having a melting point of 142-143°C.

Example P4: Preparation of 1-(3-fluoro-5,6-dichloro-2-pyridyl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione

6.8 g of 1-(3-fluoro-5-chloro-2-pyridyl-N-oxide)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione (Example P3) are added in portions to a solution, heated to 70°C, of 2.4 ml of phosphorus oxytrichloride in 20 ml of 1,2-dichloroethane and the mixture is maintained at that temperature overnight; a further 4.0 ml of phosphorus oxytrichloride is added and the mixture is heated for a further 20 hours. The mixture is then cooled, poured into ice-water and extracted with dichloroethane and the combined extracts are washed with ice-cold 2N

sodium hydroxide solution and water, dried over sodium sulfate and concentrated by evaporation. The residue is purified by means of silica gel chromatography (eluant: hexane/ethylacetate 9/1), yielding the desired title compound having a melting point of 113-115°C.

Example P5: Preparation of 1-(2-hydroxy-3-chloro-5-fluoro-pyridin-6-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione

182 g of trifluoroacetic acid anhydride are added dropwise to a solution, cooled to -30°C, of 29.6 g of 1-(3-fluoro-5-chloro-2-pyridyl-N-oxide)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione (Example P3) in 400 ml of dimethylformamide and the mixture is then stirred overnight at -30°C and on the following day at 22°C. The mixture is then freed of excess trifluoroacetic acid anhydride *in vacuo*, cooled to -5°C and cautiously neutralised first with dilute sodium hydroxide solution and then with sodium hydrogen carbonate solution. After the addition of ice-water, extraction is carried out with ethyl acetate and the combined extracts are washed with water and dried over sodium sulfate. Filtration is then carried out and the filtrate is concentrated by evaporation; the resulting residue is purified over a column of silica gel (eluant: n-hexane/ethyl acetate 8/2, with an increasing gradient with respect to ethyl acetate). The desired title compound having a melting point of 178°C is obtained.

Example P6: Preparation of 1-(2-propargyloxy-3-chloro-5-fluoro-pyridin-6-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione, 1-(2-chloro-3-propargyloxy-5-fluoro-pyridin-6-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione and 1-(1-propargyloxy-3-chloro-5-fluoro-2-pyridon-6-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione

$$\begin{array}{c} CI \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_2 \\ CH_3 \\ CH_4 \\ CH_5 \\ CH_5$$

4.5 ml of propargyl bromide are added dropwise to a suspension of 10.2 g of a mixture of 1-(2-hydroxy-3-chloro-5-fluoro-pyridin-6-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione and 1-(2-chloro-3-hydroxy-5-fluoro-pyridin-6-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione (Example P5), 7.5 g of potassium carbonate and 0.08 g of 18-crown-6 in 180 ml of acetonitrile and the mixture is then heated at 65°C overnight. Concentration by evaporation *in vacuo* is then carried out, and an ethyl acetate/ice-water mixture and 1N hydrochloric acid are added to the resulting residue until a pH of 7 is obtained; the aqueous phase is separated off and extracted with ethyl acetate and the combined organic phases are washed with water, dried over sodium sulfate, filtered and concentrated by evaporation. The residue is purified by silica gel chromatography (eluant: n-hexane/ethyl acetate 8/2), yielding the desired isomers 1-(2-propargyloxy-3-chloro-5-fluoro-pyridin-6-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione having a melting point of 121-122°C, 1-(2-chloro-3-propargyloxy-5-fluoro-pyridin-6-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione having a melting point of 69-71°C and 1-(1-propargyloxy-3-chloro-5-fluoro-2-pyridon-6-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione having a melting point of 223-224°C.

Example P7: Preparation of 1-(1-allyloxy-3-chloro-5-fluoro-2-pyridon-6-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione

A solution of 0.62 g of 1-(2-allyloxy-3-chloro-5-fluoro-pyridin-6-yl)-3-methyl-4-trifluoromethyl-pyrimidine-2,6-dione in 5 ml of dioxane is stirred at 20°C with 0.02 g of palladium(II) chloride/diacetonitrile complex until reaction is complete. The reaction mixture is then filtered over silica gel and concentrated by evaporation. The title compound is purified by silica gel chromatography (eluant: ethyl acetate/hexane). The title compound is obtained in pure form with a melting point of 115-117°C.

Example P8: Preparation of 2-(5-chloro-3-fluoro-1-oxy-pyridin-2-yl)-4,5,6,7-tetrahydro-isoindolo-1,3-dione (intermediate)

With cooling at -25° to -15°C, 15 g of trifluoroacetic acid anhydride are added in the course of 30 minutes to a suspension of 10.1 g of 2-(5-chloro-3-fluoro-pyridin-2-yl)-4,5,6,7-tetra-hydroisoindolo-1,3-dione (prepared analogously to Chem. Abstr. 114, 164251f) and 6.6 g of hydrogen peroxide/urea adduct in 100 ml of 1,2-dichloroethane. Stirring is carried out at +10°C overnight, and then a further 3.3 g of hydrogen peroxide/urea adduct is added and stirring is continued at 20°C until reaction is complete. Everything is then poured into ice-water and neutralised with aqueous 2N sodium hydroxide solution. The product is extracted with ethyl acetate, washed with water and dried. Concentration by evaporation yields a solid, which is purified by means of silica gel chromatography (eluant: hexane/ethyl acetate 7/3). The desired 2-(5-chloro-3-fluoro-1-oxy-pyridin-2-yl)-4,5,6,7-tetrahydroisoindolo-1,3-dione having a melting point of 162-164°C is obtained.

Example P9: Preparation of 2-(5-chloro-3-fluoro-6-hydroxy-pyridin-2-yl)-4,5,6,7-tetrahydro-isoindolo-1,3-dione and 2-(5-hydroxy-6-chloro-3-fluoro-pyridin-2-yl)-4,5,6,7-tetrahydro-isoindolo-1,3-dione

3.6 ml of trifluoroacetic acid anhydride are added dropwise, with cooling at -30° to -20°C, to a solution of 0.79 g of 2-(5-chloro-3-fluoro-1-oxy-pyridin-2-yl)-4,5,6,7-tetrahydroisoindolo-1,3-dione (Example P8) in 12 ml of dimethylformamide and the mixture is stirred at +10°C overnight. A further 3 ml of trifluoroacetic acid anhydride is then added dropwise and stirring is continued at +10°C for 15 hours. Concentration by evaporation is then carried out; ethyl acetate is added to the resulting residue and the mixture is rendered basic with aqueous 1N sodium hydroxide solution. Extraction is then carried out with ethyl acetate and the combined extracts are washed with water, dried and concentrated by evaporation. The residue is purified by silica gel chromatography, yielding the isomeric mixture of the two title compounds having a melting point of 190-193°C. The mixture can either be separated or further reacted directly.

In an analogous manner, and in accordance with methods as shown in the general Reaction Schemes 1-10 and in the references indicated, it is also possible to obtain the preferred compounds listed in the following Tables.

<u>Table 1</u>: A preferred group of compounds of formula I corresponds to general formula

substituents R_1 , X_1 and R_3 are given in Table A, so that 423 specific compounds of formula I_1 are disclosed.

Table 2: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_2 are disclosed.

Table 3: A further preferred group of compounds of formula I corresponds to general

formula NC
$$R_1O$$
 F F R_3O CH_3 R_3O CH_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_3 are disclosed.

Table 4: A further preferred group of compounds of formula I corresponds to general

formula
$$CH_3$$
 R_3
 R_3
 CH_3
 R_3
 CH_3
 R_3
 CH_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_4 are disclosed.

Table 5: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O}_{N} \xrightarrow{F}_{N} F$$
 (I_5) , wherein the meanings of the corresponding X_1 R_3 S CH_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_5 are disclosed.

Table 6: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 S} F_{F_1 S} F_{F_2 S} F_{F_3 S} F_{F_4 S} F_{F_5 S} F_{F_6 S} F_{F$$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_6 are disclosed.

<u>Table 7</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O} N \xrightarrow{F_1 F_1} F_1 = (I_7)$$
, wherein the meanings of the $X_1 \xrightarrow{R_3 O} CH_3$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_7 are disclosed.

<u>Table 8</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 S} F_{F_1 S} F_{F_2 S} F_{F_3 S} CH_3$$
 wherein the meanings of the corresponding

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_8 are disclosed.

Table 9: A further preferred group of compounds of formula I corresponds to general

formula
$$CH_3$$
 R_3
 R_3
 R_3
 CH_3
 R_3
 R_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_9 are disclosed.

Table 10: A further preferred group of compounds of formula I corresponds to general

formula
$$CI$$
 R_1
 R_1
 R_2
 R_3
 R_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{10} are disclosed.

<u>Table 11</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O} CH_3 \xrightarrow{F} F$$
 (I_{11}) , wherein the meanings of the corresponding $X_1 \xrightarrow{R_3 O} CH_3$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{11} are disclosed.

Table 12: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{12} are disclosed.

Table 13: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O} CN$$
 (I_{13}), wherein the meanings of the corresponding $X_1 \xrightarrow{R_3 O} CH_3$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{13} are disclosed.

Table 14: A further preferred group of compounds of formula I corresponds to general

formula
$$Br \xrightarrow{R_1 O} CH_3$$
 CN (I_{14}) , wherein the meanings of the corresponding X_1 R_3 CH_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{14} are disclosed.

Table 15: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{15} are disclosed.

Table 16: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{16} are disclosed.

Table 17: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 \circ N} N$$
 (I_{17}) , wherein the meanings of the corresponding $X_1 \xrightarrow{R_3 \circ CH_3}$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{17} are disclosed.

Table 18: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O} (I_{18})$$
, wherein the meanings of the corresponding $X_1 \xrightarrow{R_3 O} (I_{18})$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{18} are disclosed.

Table 19: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O} (I_{19})$$
, wherein the meanings of the corresponding $X_1 \xrightarrow{R_3} S$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{19} are disclosed.

Table 20: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O} CH_3$$
 F
 $K_1 O CH_3$
 $K_2 O CH_3$
 $K_3 CH_3$
 $K_3 CH_3$
 $K_4 CH_3$
 $K_5 CH_3$
 $K_5 CH_3$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{20} are disclosed.

Table 21: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1O}_{N_1} F_{F_2} F_{F_3} (I_{21})$$
, wherein the meanings of the corresponding $K_1O_{N_2} F_{F_3} F_{F_3} (I_{21})$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula l_{21} are disclosed.

Table 22: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{22} are disclosed.

Table 23: A further preferred group of compounds of formula I corresponds to general

formula
$$R_1 \cap R_2 \cap R_3 \cap R_$$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{23} are disclosed.

Table 24: A further preferred group of compounds of formula I corresponds to general

formula
$$Br \longrightarrow N$$
 $N \longrightarrow F$ F (I_{24}) , wherein the meanings of the X_1 R_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{24} are disclosed.

<u>Table 25</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$Br \longrightarrow N$$
 $N \longrightarrow F$ F (I_{25}) , wherein the meanings of the corresponding X_1 R_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{25} are disclosed.

Table 26: A further preferred group of compounds of formula I corresponds to general

formula
$$R_1 \circ F_F = (I_{26})$$
, wherein the meanings of the $X_1 \circ R_3$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{26} are disclosed.

Table 27: A further preferred group of compounds of formula I corresponds to general

formula
$$R_1O$$
 R_1O
 R_1O

the corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{27} are disclosed.

Table 28: A further preferred group of compounds of formula I corresponds to general

formula
$$R_1 O$$
 $R_1 O$
 $R_2 O$
 $R_3 O$
 R_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{28} are disclosed.

Table 29: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{29} are disclosed.

Table 30: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow N$$
 $N \longrightarrow F$ K_1 K_2 K_3 K_4 K_5 K_5 K_6 K_7 K_8 K_8

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{30} are disclosed.

Table 31: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{31} are disclosed.

Table 32: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{32} are disclosed.

Table 33: A further preferred group of compounds of formula I corresponds to general

formula
$$X_1$$
 X_2 X_3 X_4 X_4 X_5 X_4 X_5 X_5 X_6 $X_$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{33} are disclosed.

Table 34: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{34} are disclosed.

Table 35: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{35} are disclosed.

Table 36: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{36} are disclosed.

Table 37: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{37} are disclosed.

Table 38: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow N$$
 $N \longrightarrow F$ K_3 K_3 K_4 K_5 K_5 K_6 K_7 K_8 K_8

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{38} are disclosed.

Table 39: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{39} are disclosed.

Table 40: A further preferred group of compounds of formula I corresponds to general

formula
$$NC \longrightarrow N$$
 $N \longrightarrow F$ $F = (I_{40})$, wherein the meanings of the CH_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{40} are disclosed.

Table 41: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{41} are disclosed.

Table 42: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow N$$
 $N \longrightarrow N$ (I_{42}) , wherein the meanings of the corresponding

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{42} are disclosed.

Table 43: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{43} are disclosed.

Table 44: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{44} are disclosed.

Table 45: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} CH_3$$
 CH_3 $CH_$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{45} are disclosed.

Table 46: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} CI$$
 CI_{46}), wherein the meanings of the corresponding CH_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{46} are disclosed.

Table 47: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 CF_3} CI$$
 CI_{47}), wherein the meanings of the corresponding CI_{47}

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{47} are disclosed.

Table 48: A further preferred group of compounds of formula I corresponds to general

formula
$$NC$$
 R_1
 CH_3
 CH_3
 CH_3
 CH_3
 R_3
 (I_{48}) , wherein the meanings of the corresponding

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{48} are disclosed.

Table 49: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N \xrightarrow{R_2} K_3$$
 (I_{49}) , wherein the meanings of the corresponding

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{49} are disclosed.

<u>Table 50</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 CH_3} COOEt$$

$$X_1 R_3 \qquad CH_3 \qquad (I_{50}), \text{ wherein the meanings of the corresponding}$$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{50} are disclosed.

Table 51: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 NO_2} CH_3$$
 $CI \times N$ $N \times CI$ (I_{51}) , wherein the meanings of the corresponding

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{51} are disclosed.

Table 52: A further preferred group of compounds of formula I corresponds to general

formula
$$C_1$$
 R_1
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5
 C_2H_5

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{52} are disclosed.

Table 53: A further preferred group of compounds of formula I corresponds to general

formula
$$CI = \begin{pmatrix} R_1 & C_2H_5 \\ N & N \end{pmatrix}$$
 C_2H_5 C_2H_5 C_2H_5 C_2H_5

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{53} are disclosed.

Table 54: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{54} are disclosed.

Table 55: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 \ CH_3O} CH_3 \ (I_{55})$$
, wherein the meanings of the corresponding $X_1 = R_3$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{55} are disclosed.

Table 56: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 C_2H_5} Br$$
 C_{156}), wherein the meanings of the corresponding CH_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{56} are disclosed.

Table 57: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{N}_{N} N \xrightarrow{N}_{N} CH_{3}$$
 (I₅₇), wherein the meanings of the corresponding

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{57} are disclosed.

Table 58: A further preferred group of compounds of formula I corresponds to general

formula
$$CH_3$$
 R_1 R_3 (I_{58}) , wherein the meanings of the corresponding CH_3 R_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{58} are disclosed.

<u>Table 59</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 NO_2} CI$$
 C_2H_5 C_2H_5 C_2H_5 (I₅₉), wherein the meanings of the corresponding

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{59} are disclosed.

Table 60: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} CI$$
 (I_{60}) , wherein the meanings of the corresponding $X_1 = R_3$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{60} are disclosed.

<u>Table 61</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 CN} (I_{61})$$
, wherein the meanings of the corresponding $X_1 = R_3$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{61} are disclosed.

Table 62: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{62} are disclosed.

Table 63: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 CI} (I_{63})$$
, wherein the meanings of the $X_1 \xrightarrow{R_3}$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{63} are disclosed.

Table 64: A further preferred group of compounds of formula I corresponds to general

formula
$$NC \longrightarrow N$$
 $N \longrightarrow N$ $N \longrightarrow$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{64} are disclosed.

Table 65: A further preferred group of compounds of formula I corresponds to general

formula
$$CI$$
 R_1
 R_3
 R_3
 R_3
 R_3
 R_3
 R_4
 R_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{65} are disclosed.

Table 66: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 CI} CH_3$$
 (I₆₆), wherein the meanings of the $X_1 R_3$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{66} are disclosed.

Table 67: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 CH_3} CH_3$$
 (I₆₇), wherein the meanings of the $X_1 R_3$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{67} are disclosed.

Table 68: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{68} are disclosed.

Table 69: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} CH_3 CH_3$$
 (I₆₉), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{69} are disclosed.

Table 70: A further preferred group of compounds of formula I corresponds to general

formula
$$CH_3$$
 N CH_3 CH

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{70} are disclosed.

Table 71: A further preferred group of compounds of formula I corresponds to general

formula
$$NC$$
 R_1
 CH_3
 CH

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{71} are disclosed.

Table 72: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 \circ CI} (I_{72})$$
, wherein the meanings of the $X_1 \xrightarrow{R_3 \circ CH_3}$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{72} are disclosed.

Table 73: A further preferred group of compounds of formula I corresponds to general

formula
$$NC$$
 R_1
 CF_3
 CF_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{73} are disclosed.

Table 74: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} CH_3$$
 CH_3 CH_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{74} are disclosed.

Table 75: A further preferred group of compounds of formula I corresponds to general

formula
$$NC$$
 R_{1}
 CH_{3}
 CH_{3}

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{75} are disclosed.

Table 76: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{76} are disclosed.

Table 77: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 \circ} N$$
 (I_{77}) , wherein the meanings of the corresponding $X_1 \xrightarrow{R_3 \circ} N$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{77} are disclosed.

Table 78: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O} CCI_3$$
 (I₇₈), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{78} are disclosed.

Table 79: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 S} (I_{79})$$
, wherein the meanings of the corresponding $X_1 \xrightarrow{R_3 S} CF_3$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{79} are disclosed.

Table 80: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O} CH_3$$
 $CH_3 CH_3 CH_3$ (I₈₀), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{80} are disclosed.

Table 81: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N$$
 (I_{81}) , wherein the meanings of the corresponding $X_1 \xrightarrow{R_3} N$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{81} are disclosed.

Table 82: A further preferred group of compounds of formula I corresponds to general

formula
$$CH_3$$
 N R_3 O (I_{82}) , wherein the meanings of the corresponding

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{82} are disclosed.

Table 83: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{83} are disclosed.

Table 84: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{84} are disclosed.

<u>Table 85</u>: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{85} are disclosed.

Table 86: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O} F$$
 (I₈₆), wherein the meanings of the $X_1 \xrightarrow{R_3 O}$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{86} are disclosed.

Table 87: A further preferred group of compounds of formula I corresponds to general

formula
$$NC$$
 R_1
 NC
 CH_3
 (I_{87}) , wherein the meanings of the X_1
 R_3
 O

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{87} are disclosed.

Table 88: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O} CH_3$$
 (I₈₈), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{88} are disclosed.

Table 89: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{89} are disclosed.

Table 90: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N$$
 (I_{90}) , wherein the meanings of the corresponding X_1 R_3 S

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{90} are disclosed.

Table 91: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1 O} CH_3$$
 $CH_3 CH_3 CH_3$ (I₉₁), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{91} are disclosed.

Table 92: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} CH_3$$
 (I_{92}), wherein the meanings of the corresponding X_1 R_3 O

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{92} are disclosed.

Table 93: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} NH (I_{93})$$
, wherein the meanings of the corresponding $X_1 R_3 O$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{93} are disclosed.

Table 94: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} O_{N} CH_3$$
 (I₉₄), wherein the meanings of the corresponding $X_1 R_3 O_{CH_3}$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{94} are disclosed.

Table 95: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} O_{N} CH_3$$
 (I₉₅), wherein the meanings of the corresponding $X_1 \xrightarrow{R_3} O_{CH_2CH_3}$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{95} are disclosed.

Table 96: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} O CH_3$$
 $CH_2CH_2CH_3$ (I₉₆), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{96} are disclosed.

Table 97: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} O CH_3$$
 (I_{97}) , wherein the meanings of the X_1 R_3 $CH_2CH_2CH_2CH_3$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{97} are disclosed.

Table 98: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} O CH_3$$
 CH_3 CH_3 $CH_2CH_2CH_2CH_3$ CH_3 $CH_2CH_2CH_3$ CH_3 CH

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{98} are disclosed.

Table 99: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{99} are disclosed.

Table 100: A further preferred group of compounds of formula I corresponds to general

formula
$$CI = \begin{pmatrix} R_1 & O \\ N & CH_2CH_3 \end{pmatrix}$$
 (I_{100}), wherein the meanings of the $X_1 = R_3 = O$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{100} are disclosed.

Table 101: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{101} are disclosed.

Table 102: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow N \longrightarrow CH_3$$
 (I₁₀₂), wherein the meanings of the corresponding X_1 R_3 S CH_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{102} are disclosed.

Table 103: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{103} are disclosed.

<u>Table 104</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$\begin{array}{c} R_1 \\ NC \\ N \\ R_3 \end{array}$$
 $\begin{array}{c} CH_3 \\ (I_{104}), \text{ wherein the meanings of the corresponding} \end{array}$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{104} are disclosed.

Table 105: A further preferred group of compounds of formula I corresponds to general

formula
$$X_1$$
 X_1 X_3 X_4 X_4 X_4 X_5 X_6 X_6 X_8 $X_$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{105} are disclosed.

Table 106: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow N$$
 CH_3 CH_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{106} are disclosed.

<u>Table 107</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$Br \longrightarrow N \longrightarrow CH_3$$
 CH_3 CH_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{107} are disclosed.

Table 108: A further preferred group of compounds of formula I corresponds to general

formula
$$X_1$$
 X_2 X_3 X_4 X_4 X_5 X_6 X_6 X_6 X_8 $X_$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{108} are disclosed.

<u>Table 109</u>: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{109} are disclosed.

Table 110: A further preferred group of compounds of formula I corresponds to general

formula
$$CI = X_1 = X_2 = X_3 = X_1 = X_2 = X_2 = X_3 = X_3 = X_4 = X_4$$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{110} are disclosed.

Table 111: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow N$$
 $N \longrightarrow N$ OH (I_{111}) , wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{111} are disclosed.

Table 112: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{112} are disclosed.

Table 113: A further preferred group of compounds of formula I corresponds to general

formula
$$Br = \begin{pmatrix} R_1 & 0 \\ N & N \end{pmatrix}$$
 $R_3 = \begin{pmatrix} I_{113} \end{pmatrix}$, wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{113} are disclosed.

Table 114: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{114} are disclosed.

Table 115: A further preferred group of compounds of formula I corresponds to general

formula
$$NC \longrightarrow N$$
 (I₁₁₅), wherein the meanings of the corresponding $X_1 \longrightarrow R_3 \longrightarrow N$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{115} are disclosed.

Table 116: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{116} are disclosed.

Table 117: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{117} are disclosed.

Table 118: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{118} are disclosed.

Table 119: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{119} are disclosed.

Table 120: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{120} are disclosed.

Table 121: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{121} are disclosed.

Table 122: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow N$$
 $N \longrightarrow N$ O CH_3 (I_{122}) , wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{122} are disclosed.

Table 123: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow X_1 \longrightarrow X_2 \longrightarrow X_3 \longrightarrow X_1 \longrightarrow X_1 \longrightarrow X_2 \longrightarrow X_2 \longrightarrow X_3 \longrightarrow X_4 \longrightarrow X_4 \longrightarrow X_4 \longrightarrow X_4 \longrightarrow X_4 \longrightarrow X_5 \longrightarrow X_5$$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{123} are disclosed.

Table 124: A further preferred group of compounds of formula I corresponds to general

formula
$$Br = \begin{pmatrix} R_1 & 0 \\ N & N \\ X_1 & R_3 & 0 \end{pmatrix}$$
 (I₁₂₄), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{124} are disclosed.

Table 125: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{125} are disclosed.

Table 126: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{126} are disclosed.

Table 127: A further preferred group of compounds of formula I corresponds to general

formula
$$CI = X_1 = X_2 = X_3 = X_1 = X_3 = X_1 = X_2 = X_2 = X_3 = X_3 = X_4 = X_4$$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{127} are disclosed.

Table 128: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow N$$
 $N \longrightarrow N$ $O \longrightarrow CH_3$ (I₁₂₈), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{128} are disclosed.

Table 129: A further preferred group of compounds of formula I corresponds to general

formula
$$C_1$$
 X_1
 X_1
 X_3
 X_1
 X_3
 X_4
 X_4
 X_4
 X_5
 X_6
 X_7
 X_8
 $X_$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{129} are disclosed.

Table 130: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow N$$
 $N \longrightarrow N$ $N \longrightarrow$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{130} are disclosed.

Table 131: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow K_1 O$$
 $K_1 O$
 $K_2 O$
 $K_3 O$
 $K_4 O$
 $K_4 O$
 $K_5 O$
 $K_6 O$
 $K_7 O$
 $K_8 O$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{131} are disclosed.

Table 132: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{132} are disclosed.

Table 133: A further preferred group of compounds of formula I corresponds to general

formula
$$NC \longrightarrow N$$
 $NC \longrightarrow N$ NC

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{133} are disclosed.

Table 134: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{134} are disclosed.

Table 135: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow N$$
 (I_{135}) , wherein the meanings of the corresponding $X_1 \longrightarrow R_3 \longrightarrow N$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{135} are disclosed.

Table 136: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{136} are disclosed.

Table 137: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \longrightarrow N$$
 $N \longrightarrow N$ $N \longrightarrow N$ wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{137} are disclosed.

<u>Table 138</u>: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{138} are disclosed.

Table 139: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{139} are disclosed.

Table 140: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{140} are disclosed.

Table 141: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N_{N-CH_3} N_{CH_3}$$
 (I₁₄₁), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{141} are disclosed.

Table 142: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N \xrightarrow{N} CH_3$$
 (I_{142}) , wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{142} are disclosed.

Table 143: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} CH_3$$
 CH_3 CH_3 CH_3 (I₁₄₃), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{143} are disclosed.

Table 144: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{144} are disclosed.

Table 145: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{145} are disclosed.

Table 146: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{146} are disclosed.

Table 147: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{147} are disclosed.

Table 148: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N \xrightarrow{CH_3} CH_3$$
 (I₁₄₈), wherein the meanings of the CH_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{148} are disclosed.

Table 149: A further preferred group of compounds of formula I corresponds to general

formula
$$NC \longrightarrow N$$
 $NC \longrightarrow N$ NC

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{149} are disclosed.

Table 150: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N \xrightarrow{N} (I_{150})$$
, wherein the meanings of the corresponding $X_1 \xrightarrow{R_3} 0$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{150} are disclosed.

Table 151: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{151} are disclosed.

Table 152: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{152} are disclosed.

Table 153: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N \xrightarrow{N} S (I_{153})$$
, wherein the meanings of the corresponding $X_1 \xrightarrow{R_3} O$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{153} are disclosed.

Table 154: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N \xrightarrow{N} N = N$$
 (I₁₅₄), wherein the meanings of the corresponding

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{154} are disclosed.

<u>Table 155</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} CH_3$$
 CH_3 $CH_$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{155} are disclosed.

Table 156: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{156} are disclosed.

Table 157: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{157} are disclosed.

Table 158: A further preferred group of compounds of formula I corresponds to general

formula
$$Br \xrightarrow{R_1} O_{N - CH_3} CH_3$$
 (I₁₅₈), wherein the meanings of the corresponding $X_1 - R_3 = 0$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{158} are disclosed.

Table 159: A further preferred group of compounds of formula I corresponds to general

formula
$$NC \longrightarrow NH$$
 $NC \longrightarrow NH$ $NC \longrightarrow N$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{159} are disclosed.

Table 160: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} (N_1)^{CH(CH)_3} (I_{160})$$
, wherein the meanings of the X_1 R_3 O

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{160} are disclosed.

Table 161: A further preferred group of compounds of formula I corresponds to general

formula
$$CI = X_1 \cap X_1 \cap X_2 \cap X_1 \cap X_1 \cap X_2 \cap X_1 \cap X_2 \cap X_2 \cap X_3 \cap X_4 \cap X_4 \cap X_4 \cap X_5 \cap X_5$$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{161} are disclosed.

Table 162: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} CH_3$$
 CH_3 $CH_$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{162} are disclosed.

Table 163: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} O \xrightarrow{N} CH_3$$
 (I₁₆₃), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{163} are disclosed.

Table 164: A further preferred group of compounds of formula I corresponds to general

formula
$$CH_3$$
 N
 CH_3
 CH

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{164} are disclosed.

Table 165: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{165} are disclosed.

Table 166: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{166} are disclosed.

Table 167: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{167} are disclosed.

Table 168: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{168} are disclosed.

Table 169: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{169} are disclosed.

Table 170: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N \xrightarrow{N} O$$
 (I_{170}) , wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{170} are disclosed.

Table 171: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{171} are disclosed.

<u>Table 172</u>: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{172} are disclosed.

Table 173: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{173} are disclosed.

Table 174: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} CH_3$$
 CH_3 $CH_$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{174} are disclosed.

Table 175: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{175} are disclosed.

Table 176: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{176} are disclosed.

Table 177: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{N}_{N} = \begin{pmatrix} N & N & N \\ N & N & N \\ N & N & N \end{pmatrix}$$
, wherein the meanings of the corresponding X_1 X_2 X_3 X_4 X_4 X_4 X_5 X_5 X_5

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{177} are disclosed.

Table 178: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{178} are disclosed.

Table 179: A further preferred group of compounds of formula I corresponds to general

formula
$$R_1$$
 R_2 R_3 R_3 R_3 R_3 R_4 R_3 R_4 R_5 $R_$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{179} are disclosed.

Table 180: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{180} are disclosed.

<u>Table 181</u>: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{181} are disclosed.

Table 182: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{182} are disclosed.

Table 183: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{183} are disclosed.

Table 184: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{184} are disclosed.

Table 185: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{185} are disclosed.

Table 186: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{186} are disclosed.

Table 187: A further preferred group of compounds of formula I corresponds to general

formula
$$CH_3$$
 X_1
 R_3
 R_3
 (I_{187}) , wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{187} are disclosed.

Table 188: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N \xrightarrow{N_N} S$$
 (I₁₈₈), wherein the meanings of the corresponding $X_1 \xrightarrow{R_3}$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{188} are disclosed.

<u>Table 189</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} O_{N} CH_3$$
 CH_3 CH_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{189} are disclosed.

Table 190: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{190} are disclosed.

Table 191: A further preferred group of compounds of formula I corresponds to general

formula
$$CH_3$$
 N N CH_3 CH_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{191} are disclosed.

Table 192: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} CHF_2$$
 C_2H_5 (I_{192}) , wherein the meanings of the corresponding X_1 R_3

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{192} are disclosed.

Table 193: A further preferred group of compounds of formula I corresponds to general

formula
$$NC \longrightarrow N \longrightarrow N \longrightarrow CHF_2$$

$$X_1 \longrightarrow R_3 \longrightarrow R_3 \longrightarrow CHF_2$$

$$(I_{193}), \text{ wherein the meanings of the corresponding}$$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{193} are disclosed.

Table 194: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N_{N-CHF_2} CH_3$$
 (I_{194}) , wherein the meanings of the corresponding $X_1 = R_3$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{194} are disclosed.

Table 195: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N_{N} CHF_2$$
 CHF_2
 CHF_3
 $CHF_$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{195} are disclosed.

Table 196: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N \xrightarrow{CH_3} CF_3$$
 (I₁₉₆), wherein the meanings of the corresponding

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{196} are disclosed.

Table 197: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N \xrightarrow{CH(CH_3)_2} (I_{197})$$
, wherein the meanings of the X_1 R_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{197} are disclosed.

Table 198: A further preferred group of compounds of formula I corresponds to general

formula
$$CF_3$$
 N
 N
 CHF_2
 CH_3
 (I_{198}) , wherein the meanings of the X_1
 R_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{198} are disclosed.

<u>Table 199</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N_{N} CH_3$$
 (I₁₉₉), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{199} are disclosed.

Table 200: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N_{N} CH_3$$
 (I_{200}) , wherein the meanings of the X_1 R_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{200} are disclosed.

Table 201: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N_{N} \xrightarrow{N} CH_3 CI$$
 (I₂₀₁), wherein the meanings of the X_1 R_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{201} are disclosed.

Table 202: A further preferred group of compounds of formula I corresponds to general

formula
$$CH_3$$
 N N CH_3 (I_{202}) , wherein the meanings of the X_1 R_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{202} are disclosed.

Table 203: A further preferred group of compounds of formula I corresponds to general

formula
$$CF_3O \xrightarrow{R_1} N_{N-CH_3} CHF_2$$
 $X_1 R_3$ (I₂₀₃), wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{203} are disclosed.

Table 204: A further preferred group of compounds of formula I corresponds to general

formula
$$CI \xrightarrow{R_1} N_N$$
 N_N N_N

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{204} are disclosed.

Table 205: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{205} are disclosed.

Table 206: A further preferred group of compounds of formula I corresponds to general

formula
$$Br \xrightarrow{R_1} N \xrightarrow{N} N \xrightarrow{N} CHF_2$$
 (I₂₀₆), wherein the meanings of the corresponding

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{206} are disclosed.

Table 207: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{207} are disclosed.

Table 208: A further preferred group of compounds of formula I corresponds to general

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{208} are disclosed.

Table 209: A further preferred group of compounds of formula I corresponds to general

formula
$$X_1$$
 X_1 X_3 X_4 X_4 X_4 X_4 X_4 X_4 X_5 X_6 X_6 X_8 $X_$

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{209} are disclosed.

<u>Table 210</u>: A further preferred group of compounds of formula I corresponds to general

formula
$$N = \begin{bmatrix} R & O & CH_3 \\ N & N & F \end{bmatrix}$$
 $K = \begin{bmatrix} CH_3 & F \\ N & N \end{bmatrix}$ $K = \begin{bmatrix} CH_3 & F \\ N & N \end{bmatrix}$ wherein the meanings of the

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{210} are disclosed.

Table 211: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{211} are disclosed.

Table 212: A further preferred group of compounds of formula i corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{212} are disclosed.

Table 213: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{213} are disclosed.

Table 214: A further preferred group of compounds of formula I corresponds to general

formula
$$(CH_3)_3C$$
 $(CH_3)_3C$
 $(CH_3)_3$

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{214} are disclosed.

Table 215: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{215} are disclosed.

Table 216: A further preferred group of compounds of formula I corresponds to general

formula
$$F$$
 X_1
 X_1
 X_3
 X_1
 X_3
 X_4
 X_3
 X_4
 X_3
 X_4
 X_4
 X_4
 X_5
 X_4
 X_5
 X_6
 X_6
 X_6
 X_6
 X_7
 X_8
 X_8

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{216} are disclosed.

Table 217: A further preferred group of compounds of formula I corresponds to general

formula
$$N$$
 O
 N
 N
 N
 CHF_2
 CHF_3
 CHF_3

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{217} are disclosed.

Table 218: A further preferred group of compounds of formula I corresponds to general

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{218} are disclosed.

<u>Table 219:</u> A preferred group of compounds of formula I corresponds to general formula

substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{219} are disclosed.

Table 220: A preferred group of compounds of formula I corresponds to general formula

corresponding substituents R_1 , X_1 and R_3 are indicated in Table A, so that 423 specific compounds of formula I_{220} are disclosed.

Table A

Table A	T		
Comp. No.	R ₁	X ₁	R ₃
.001	Н	0	CH₃
.002	F	0	CH₃
.003	CI	0	CH₃
.004	F	0	CH₂CH₃
.005	CI	0	CH₂CH₃
.006	Н	0	CH₂CH₃
.007	F	0	CH₂CH₂CH₃
.008	CI	0	CH₂CH₂CH₃
.009	H	0	CH ₂ CH ₂ CH ₃
.010	F	0	CH₂CH₂CH₃
.011	CI	0	CH₂CH₂CH₂CH₃
.012	F	0	CH₂CH₂CH₂CH₃
.013	CI	0	CH ₂ CH ₂ CH ₂ CH ₃
.014	F	0	CH₂CH₂CH₂CH₂CH₃
.015	F	0	CH ₂ CH ₂ CH(CH ₃) ₂
.016	CI	0	CH ₂ CH ₂ CH(CH ₃) ₂
.017	Н	0	CH ₂ CH ₂ CH(CH ₃) ₂
.018	F	0	CH ₂ CH(CH ₃)CH ₂ CH ₃
.019	CI	0	CH₂CH(CH₃)CH₂CH₃
.020	Н	0	CH₂CH(CH₃)CH₂CH₃
.021	F	0	CH ₂ CH(CH ₃)CH ₂ CH ₂ CH ₃
.022	F	0	CH₂CH₂CH(CH₃)CH₂CH₃
.023	F	0	CH₂CH₂CH(CH₃)₂
.024	F	0	CH(CH₃)CH₂CH₂CH₃
.025	CI	0	CH(CH₃)CH₂CH₂CH₃
.026	Н	0	CH(CH₃)CH₂CH₂CH₃
.027	F	0	CH₂C(CH₃)₃
.028	CI	0	CH₂C(CH₃)₃
.029	Н	0	CH₂CH(CH₃)₂
.030	CI	0	CH ₂ CH(CH ₃) ₂
.031	F	0	CH ₂ CH(CH ₃) ₂
.032	F	0	CH ₂ C(CH ₃) ₂ CH ₂ CH ₃
.033	CI	0	CH ₂ C(CH ₃) ₂ CH ₂ CH ₃
.034	Н	0	CH ₂ C(CH ₃) ₂ CH ₂ CH ₃

Comp. No.	R ₁	X ₁	R ₃
.035	F	0	CH₂CH₂C(CH₃)₃
.036	CI	0	CH ₂ CH ₂ C(CH ₃) ₃
.037	F	0	CH₂CH₂CHCH₂
.038	F	0	CH₂CH₂CH₃
.039	F	0	CH(CH ₃) ₂
.040	CI	0	CH(CH ₃) ₂
.041	Н	0	CH(CH ₃) ₂
.042	F	0	CH₂CF₃
.043	CI	0	CH₂CF ₃
.044	Н	0	CH₂CF₃
.045	F	0	CH₂CCI₃
.046	F	0	CH₂CH₂CF₃
.047	F	0	CH₂CH₂CH(OH)CH₃
.048	F	0	CH₂CH(OH)CH₂CH₃
.049	CI	0	CH₂CH(OH)CH₂CH₃
.050	F	0	CH₂CH(OH)CH₃
.051	Н	0	CH₂CH₂CHCICH₃
.052	CI	0	CH₂CH₂CHClCH₃
.053	F	0	CH₂CH₂CHClCH₃
.054	F	0	CH₂CH₂CHFCH₃
.055	F	0	CH₂CHFCH₂CH₃
.056	CI	0	CH₂CHFCH₂CH₃
.057	Н	0	CH₂CHFCH₂CH₃
.058	F	0	CH₂CHCICH₂CH₃
.059	F	0	CH₂CH₂F
.060	CI	0	CH₂CH₂F
.061	F	0	CH₂CHF₂
.062	Н	0	CH₂CHCH₂
.063	CI	0	CH₂CHCH₂
.064	F	0	CH₂CHCH₂
.065	F	0	CH₂CH(CH₃)CH₂
.066	F	0	CH₂CHCH(CH₃)
.067	CI	0	CH₂CH₂OH
.068	F	0	CH₂CH₂OH
.069	F	0	CH₂CHCHCI

Comp. No.	R ₁	X ₁	R ₃
.070	CI	0	CH₂CHCHCI
.071	F	0	CH₂OCH₂C ₆ H ₅
.072	Н	0	CH₂CCH
.073	CI	0	CH₂CCH
.074	F	0	CH₂CCH
.075	F	0	CH₂CH₂CCH
.076	CI	0	CH ₂ CH ₂ C ₆ H ₅
.077	F	0	CH ₂ CH ₂ C ₆ H ₅
.078	F	0	CH ₂ CH ₂ CH ₂ C ₆ H ₅
.079	F	0	CH ₂ CH ₂ CH(CH ₃)C ₆ H ₅
.080	F	0	CH ₂ CH ₂ CH ₂ CH ₂ (p-F-C ₆ H ₄)
.081	Н	0	CH₂C ₆ H ₅
.082	CI	0	CH₂C ₆ H ₅
.083	F	0	CH₂C ₆ H ₅
.084	F	0	CH ₂ (o-F-C ₆ H ₄)
.085	Н	0	$CH_2(p-Cl-C_6H_4)$
.086	F	0	CH₂(m-CF₃-C ₆ H₅)
.087	Н	0	CH₂CN
.088	CI	0	CH₂CN
.089	F	0	CH₂CN
.090	F	0	CH₂CH₂CN
.091	F	0	cyclopropyl
.092	F	0	cyclopentyl
.093	F	0	CH₂-cyclopentyl
.094	F	0	CH₂-cyclopropyl
.095	F	0	CH₂CH₂CI
.096	F	0	CH₂CHCl₂
.097	Н	0	CH₂OCH₃
.098	CI	0	CH₂OCH₃
.099	F	0	CH₂OCH₃
.100	F	0	CH₂CH₂OCH₃
.101	F	0	CH ₂ CH ₂ OCH ₂ CH ₃
.102	F	0	CH₂CH(CH₃)OCH₃
.103	Н	0	CH ₂ CH ₂ OCH ₂ CH ₂ OCH ₃
.104	CI	0	CH ₂ CH ₂ OCH ₂ CH ₂ OCH ₃

Comp. No.	R ₁	X ₁	R ₃
.105	F	0	CH₂CH₂OCH₂CH₂OCH₃
.106	Н	0	CH₂SCH₃
.107	CI	0	CH₂SCH₃
.108	F	0	CH₂SCH₃
.109	н	0	CH₂S(O)CH₃
.110	CI	0	CH₂S(O)CH₃
.111	F	0	CH₂S(O)CH₃
.112	Н	0	CH₂S(O)₂CH₃
.113	CI	0	CH₂S(O)₂CH₃
.114	F	0	CH₂S(O)₂CH₃
.115	F	0	CH₂SCH₂CH₃
.116	F	0	CH₂CH₂SCH₃
.117	F	0	CH₂CH₂SCH₂CH₃
.118	CI	0	CH₂CH₂SCH₂CH₃
.119	Н	0	CH₂CH₂SCH₂CH₃
.120	CI	0	CH₂CH₂SCH₃
.121	Н	0	CH₂CH₂SCH₃
.122	F	0	CH ₂ CH ₂ S(O)CH ₃
.123	F	0	CH₂CH₂S(O)₂CH₃
.124	CI	0	CH ₂ CH ₂ S(O)CH ₃
.125	CI	0	CH₂CH₂S(O)₂CH₃
.126	F	0	CH ₂ CH ₂ S(O)CH ₂ CH ₃
.127	CI	0	CH ₂ CH ₂ S(O)CH ₂ CH ₃
.128	Н	0	CH ₂ CH ₂ S(O)CH ₂ CH ₃
.129	F	0	CH ₂ CH ₂ S(O) ₂ CH ₂ CH ₃
.130	CI	0	CH₂CH₂S(O)₂CH₂CH₃
.131	Н	0	CH ₂ CH ₂ S(O) ₂ CH ₂ CH ₃
.132	F	0	CH₂CH(CH₃)SCH₃
.133	Н	0	CH₂COOH
.134	CI	0	CH₂COOH
.135	F	0	CH₂COOH
.136	F	0	CH₂COOCH₃
.137	Н	0	CH₂COOCH₂CH₃
.138	CI	0	CH₂COOCH₂CH₃
.139	F	0	CH₂COOCH₂CH₃

Comp. No.	R₁	X ₁	R ₃
.140	F	0	CH₂COOC(CH₃)₃
.141	F	0	CH₂COOCH₂CHCH₂
.142	F	0	CH₂COOCH₂CCH
.143	F	0	CH₂COOCH₂C ₆ H ₅
.144	Н	0	CH₂CHO
.145	CI	0	CH₂CHO
.146	F	0	CH₂CHO
.147	Н	0	CH₂C(O)CH₃
.148	CI	0	CH₂C(O)CH₃
.149	F	0	CH₂C(O)CH₃
.150	F	0	CH₂COSCH₂CH₃
.151	Н	0	CH ₂ COSCH(CH ₃) ₂
.152	CI	0	CH₂COSCH(CH₃)₂
.153	F	0	CH₂COSCH(CH₃)₂
.154	F	0	CH₂COSCH₂C ₆ H ₅
.155	F	0	CH₂CONH₂
.156	F	0	CH₂CON(CH₃)₂
.157	CI	0	CH₂CON(CH₃)₂
.158	F	0	CH ₂ CON(CH ₂ CH ₃) ₂
.159	CI	0	CH₂CON(CH₂CH₃)₂
.160	Н	0	CH ₂ CON(CH ₂ CH ₃) ₂
.161	F	0	CH₂OCH₂C ₆ H ₅
.162	CI	0	CH₂CONHCH₂CCH
.163	F	0	CH₂CONHCH₂CCH
.164	CI	0	CH₂CH₂COOH
.165	F	0	CH₂CH₂COOH
.166	F	0	CH₂CH₂COOCH₂CH₃
.167	Н	0	CH₂CH₂CN
.168	CI	0	CH₂CH₂CN
.169	F	0	CH₂CH₂CN
.170	F	0	CH₂CH(CH₃)CN
.171	CI	0	CH(CH₃)CH₂CN
.172	CI	0	CH₂CH₂CHO
.173	F	0	CH₂CH₂CHO
.174	F	0	CH₂CH₂C(O)CH₃

Comp. No.	R₁	X ₁	R ₃
.175	CI	0	CH₂CH₂C(O)CH₃
.176	F	0	CH₂COCH₂CH₃
.177	CI	0	CH₂COCH₂CH₃
.178	Н	0	CH₂COCH₂CH₃
.179	F	0	CH₂COCH₂CH₂CH₃
.180	F	0	CH₂CH₂COCH₂CH₃
.181	F	0	CH₂CH₂COCH₂CF₃
.182	F	0	CH₂CHCICOCH₂CH₃
.183	F	0	CH₂CH₂COCHCICH₃
.184	F	0	CH₂CH(CH₃)COOCH₃
.185	F	0	CH₂CH₂COOCH₃
.186	F	0	CH₂CH₂CH₂COSCH₂CH₃
.187	F	0	CH₂CH₂CON(CH₃)₂
.188	F	0	CH₂CH₂CH(CH₃)COOCH₂CH₃
.189	Н	0	CH₂CH(OH)COOH
.190	CI	0	CH₂CH(OH)COOH
.191	F	0	CH₂CH(OH)COOH
.192	CI	0	CH₂CH(CI)COOH
.193	F	0	CH₂CH(CI)COOH
.194	CI	0	CH₂CH(CI)COOCH₂CH₃
.195	F	0	CH₂CH(CI)COOCH₂CH₃
.196	F	0	CH₂CH(CI)COOH
.197	F	0	CH₂C(CH₃)(CI)COOH
.198	F	0	CH₂CH(CI)COOCH₂CHCH₂
.199	F	0	CH₂CH(CI)COOCH₂CCH
.200	F	0	CH₂CH(CI)COOCH₂C ₆ H ₅
.201	F	0	CH₂CH(CI)C(O)SCH(CH₃)₂
.202	F	0	CH₂CH(CI)C(O)NH(CH₂CCH)
.203	F	0	$CH_2CH(CH_3)C(O)N(CH_3)(CH_2CHCH_2)$
.204	F	0	CH₂CH(Br)COOC(CH₃)₃
.205	F	0	CH ₂ CH(Br)COOCH ₂ CHCH ₂
.206	F	0	CH ₂ COOCH ₂ CH ₂ CI
.207	F	0	CH ₂ COOCH ₂ CF ₃
.208	Н	0	CH ₂ <0

Comp. No.	R ₁	X ₁	R ₃
.209	Н	0	CH ₂ O
.210	CI	0	CH ₂ <0
.211	F	0	CH ₂ <0
.212	F	0	CH ₂ O
.213	F	0	S(O) ₂ CH ₃
.214	F	0	S(O) ₂ CH ₂ CH ₃
.215	CI	0	S(O) ₂ CF ₃
.216	CI	0	S(O) ₂ CH ₂ CH ₃
.217	F	0	S(O) ₂ CH(CH ₃) ₂
.218	Н	0	C(O)CH₃
.219	CI	0	C(O)CH₃
.220	F	0	C(O)CH₃
.221	F	0	C(O)CF ₃
.222	F	0	C(O)CH₂CH₃
.223	CI	0	ОН
.224	F	0	ОН
.225	Н	0	OCH₃
.226	CI	0	OCH₃
.227	F	0	OCH₃
.228	Н	0	OCH₂CH₃
.229	Cl	0	OCH₂CH₃
.230	F	0	OCH₂CH₃
.231	F	0	OCH₂CH(CH₃)₂
.232	F	0	OCF ₃
.233	F	0	OCHF₂
.234	F	0	OCH ₂ CHCH ₂
.235	F	0	OCH ₂ C(CH ₃)CH ₂
.236	F	0	OCH₂CHCHCl
.237	CI	0	OCH₂OCH₃
.238	F	0	OCH₂OCH₃
.239	F	0	OCH₂SCH₃

Comp. No.	R ₁	X ₁	R ₃
.240	F	0	OCH₂CCH
.241	F	0	OCH₂COOH
.242	F	0	OCH₂COOCH₃
.243	F	0	OCH₂COOCH₂CH₃
.244	F	0	OCH₂COOCH(CH₃)₂
.245	CI	0	OCH(CH₃)COOH
.246	F	0	OCH(CH₃)COOH
.247	F	0	OCH(CH₃)COOCH₂CH₃
.248	F	0	OCH(CH₃)COOCH₂CCH
.249	F	0	OCH(CH₃)COOCH₂CHCH₂
.250	F	0	OCH₂COSCH₂CH₃
.251	F	0	OCH₂COSCH(CH₃)₂
.252	F	0	OCH ₂ COSCH ₂ C ₆ H ₅
.253	F	0	OCH₂CONH₂
.254	F	0	OCH₂CON(CH₃)₂
.255	CI	0	OCH₂CONHCH₂CCH
.256	F	0	OCH₂CONHCH₂CCH
.257	F	0	OCH ₂ C ₆ H ₅
.258	F	0	$OCH_2(p-CH_3O-C_6H_4)$
.259	F	0	$OCH_2(o-F-C_6H_4)$
.260	CI	0	$OCH_2(m-CF_3-C_6H_4)$
.261	F	0	OCH ₂ CH ₂ C ₆ H ₅
.262	Н	0	OCH₂CN
.263	F	0	OCH₂CN
.264	F	0	OCH₂CH₂CI
.265	CI	0	OCH₂CH₂OH
.266	F	0	OCH ₂ CH ₂ OH
.267	Н	0	OCH ₂ CH ₂ CN
.268	CI	0	OCH ₂ CH ₂ CN
.269	F	0	OCH₂CH₂CN
.270	CI	0	OCH ₂ CH(OCH ₃)(CH ₃)
.271	F	0	OCH₂CH(OCH₃)(CH₃)
.272	Н	0	OC(O)CH ₃
.273	CI	0	OC(O)CH ₃
.274	F	0	OC(O)CH ₃

Comp. No.	R ₁	X ₁	R ₃
.275	Н	S	CH₃
.276	CI	S	CH₃
.277	F	S	CH₃
.278	Н	S	CH₂CH₃
.279	CI	S	CH₂CH₃
.280	F	S	CH₂CH₃
.281	F	S	CH₂CH₂CH₃
.282	F	S	CH₂CH(CH₃)₂
.283	F	S	CH₂CH₂CF₃
.284	F	S	CH(CH ₃) ₂
.285	F	S	CH₂CH(CH₃)₂
.286	F	S	CH₂CH(CI)CH₃
.287	CI	S	CH₂CHCH₂
.288	F	S	CH₂CHCH₂
.289	F	S	CH₂C(CH₃)CH₂
.290	Н	S	CH₂CCH
.291	CI	S	CH₂CCH
.292	F	S	CH₂CCH
.293	F	S	CH₂CH₂CCH
.294	F	S	CH(CH₃)CCH
.295	Н	S	CH₂CH₂OH
.296	CI	S	CH₂CH₂OH
.297	F	S	CH₂CH₂OH
.298	F	S	CH₂CH(OH)CH₃
.299	Н	S	CH₂C ₆ H ₅
.300	CI	S	CH₂C ₆ H ₅
.301	F	S	CH₂C ₆ H ₅
.302	CI	S	CH ₂ (o-F-C ₆ H ₄)
.303	F	S	$CH_2(o-F-C_6H_4)$
.304	F	S	CH₂(m-CF₃-C ₆ H₄)
.305	F	S	$CH_2(p-CH_3-C_6H_4)$
.306	F	S	$CH_2(2,4-di-F-C_6H_3)$
.307	F	S	$CH_2CH_2CH(CH_3)C_6H_5$
.308	F	S	$CH_2CH_2CH_2CH_2(p-F-C_6H_4)$
.309	CI	S	CH ₂ CN

Comp. No.	R ₁	X ₁	R ₃
.310	F	S	CH₂CN
.311	F	S	cyclopropyl
.312	CI	S	CH₂-cyclopropyl
.313	F	S	CH₂-cyclopropyl
.314	F	S	CH₂CI
.315	н	S	CH₂OCH₃
.316	CI	S	CH₂OCH₃
.317	F	S	CH₂OCH₃
.318	F	S	CH₂OCH₂CHCH₂
.319	F	S	CH₂CH₂OCH₃
.320	F	S	CH ₂ CH(OCH ₃)CH ₃
.321	F	S	CH₂CH(OCH₂CCH)CH₃
.322	Н	S	CH₂CH₂OCH₂CH₂OCH₃
.323	CI	S	CH₂CH₂OCH₂CH₂OCH₃
.324	F	S	CH₂CH₂OCH₂CH₂OCH₃
.325	Н	S	CH₂SCH₃
.326	CI	S	CH₂SCH₃
.327	F	S	CH₂SCH₃
.328	F	S	CH₂SCH₂CHCH₂
.329	F	S	CH₂SCH₂CCH
.330	F	S	CH₂CH₂SCH₃
.331	F	S	CH₂CH₂S(O)CH₃
.332	F	S	CH ₂ CH ₂ S(O) ₂ CH ₃
.333	F	S	CH₂COOH
.334	F	S	CH₂COOCH₃
.335	F	S	CH₂COOCH₂CH₃
.336	F	S	CH₂COOC(CH₃)₃
.337	F	S	CH ₂ COOCH ₂ C ₆ H ₅
.338	F	S	$CH_2COOCH_2(p-CI-C_6H_4)$
.339	F	S	CH₂C(O)SCH₃
.340	F	S	CH ₂ C(O)SCH(CH ₃) ₂
.341	F	S	$CH_2C(O)SCH_2C_6H_5$
.342	F	S	CH ₂ C(O)NH ₂
.343	F	S	CH₂C(O)NH(CH₃)
.344	CI	S	CH₂C(O)NH(CH₂CCH)

Comp. No.	R ₁	X ₁	R ₃
.345	F	S	CH ₂ C(O)NH(CH ₂ CCH)
.346	F	S	CH₂C(O)N(CH₂CH₃)₂
.347	F	S	CH₂CHO
.348	F	S	CH₂C(O)CH₃
.349	н	S	CH₂CH₂COOH
.350	CI	S	CH₂CH₂COOH
.351	F	S	CH₂CH₂COOH
.352	F	S	CH₂CH₂COOCH₃
.353	F	S	CH₂CH₂COOCH₂C6H5
.354	CI	S	CH₂CH₂C(O)SCH₂CH₃
.355	F	S	CH ₂ CH ₂ C(O)SCH ₂ CH ₃
.356	F	S	CH₂CH(OH)COOH
.357	F	S	CH₂CH(CI)COOH
.358	CI	S	CH₂CH(CI)COOCH₂CH₃
.359	F	S	CH₂CH(CI)COOCH₂CH₃
.360	F	S	CH₂CH(CI)COOH
.361	F	S	CH₂C(CH₃)(CI)COOH
.362	F	S	CH₂CH(CI)COOCH₂CHCH₂
.363	CI	S	CH₂CH(CI)COOCH₂CCH
.364	F	S	CH₂CH(CI)COOCH₂CCH
.365	F	S	CH₂CH(CI)COOCH₂C ₆ H₅
.366	F	S	CH₂CH(Br)COOH
.367	F	S	CH ₂ CH(CI)C(O)SCH(CH ₃) ₂
.368	F	S	CH₂CH(CI)C(O)NH(CH₂CCH)
.369	F	S	$CH_2CH(CH_3)C(O)N(CH_3)(CH_2CHCH_2)$
.370	F	S	CH₂CH₂C(O)NH(CH₂CCH)
.371	Н	S	CH ₂
.372	CI	S	CH ₂
.373	F	S	CH ₂ O
.374	CI	S	CH ₂ <0
.375	F	S	CH ₂

Comp. No.	R ₁	X ₁	R ₃
.376	F	S	ОН
.377	н	S	OCH₃
.378	CI	S	OCH₃
.379	F	S	OCH₃
.380	F	S	OCH₂CH₃
.381	CI	S	OCH₂CH(CH₃)₂
.382	F	S	OCH₂CH(CH₃)₂
.383	F	S	OCH(CH ₃) ₂
.384	F	S	OCF₃
.385	Н	S	OCH₂OCH₃
.386	CI	S	OCH₂OCH₃
.387	F	S	OCH₂OCH₃
.388	F	S	OCH₂SCH₃
.389	CI	S	OCH₂CHCH₂
.390	F	S	OCH₂CHCH₂
.391	CI	S	OCH₂CCH
.392	F	S	OCH₂CCH
.393	F	S	OCH(CH₃)CHCH₂
.394	F	S	OCH(CH₃)CCH
.395	F	S	OCH₂CHCH(CI)
.396	F	S	OCH₂COOH
.397	F	S	OCH₂COOCH₂CH₃
.398	F	S	OCH(CH₃)COOH
.399	F	S	OCH(CH₃)COOCH₂CCH
.400	F	S	OCH ₂ C(O)NH ₂
.401	F	S	OCH₂C(O)NH(CH₃)
.402	F	S	OCH₂C(O)NH(CH₂CCH)
.403	F	S	OCH₂C(O)SCH₃
.404	F	S	OCH₂C(O)SCH₂CH₃
.405	F	S	OCH₂C(O)SCH(CH₃)₂
.406	CI	S	OCH ₂ C(O)SCH ₂ C ₆ H ₅
.407	F	S	OCH(CH ₃)C(O)SCH ₂ C ₆ H ₅
.408	F	S	OCH₂CH₂OH
.409	F	S	OCH₂CH(CH₃)OH
.410	F	S	OCH ₂ CH ₂ Cl

Comp. No.	R ₁	X ₁	R ₃
.411	CI	S	OCH₂CH₂CN
.412	F	S	OCH₂CH₂CN
.413	CI	S	OCH₂CH₂CF₃
.414	F	S	OCH₂CH₂CF₃
.415	F	S	OCH₂CH(OH)(C ₆ H₅)
.416	F	0	CH₂COCH₃
.417	F	0	CH₂CONHCH₂CH=CH₂
.418	CI	0	CH ₂ CONHCH ₂ CH=CH ₂
.419	CI	S	CH₂CONHCH₂CH₃
.420	CI	0	CH₂CONHCH₂CH₃
.421	F	0	CH₂CONHCH₂CH₃
.422	F	0	CH₂CONHCH₃
.423	CI	0	CH₂CONHCH₃

<u>Table B:</u> Prepared compounds from the preceding Tables with physico-chemical data. The figure before the point indicates the number of the Table, e.g. 1.002 indicates in Table 1 compound No. 002 of Table A.

Comp. No.	physical data
1.002	m.p. 159-160°C
1.007	m.p. 123-125°C
1.064	m.p. 115-116°C
1.071	nD(30°C) 1.5431
1.074	m.p. 218-220°C
1.139	nD(30°C) 1.5131
34.074	¹ H-NMR (CDCl ₃): 8,14 ppm (s, 1H); 7,72 ppm (d, 1H);
	7,36 ppm (s, 1H); 4,90 ppm (s, 2H); 2,21 ppm (s, 1H)

Examples of specific formulations for compounds of formula I, such as emulsifiable concentrates, solutions, wettable powders, coated granules, extruder granules, dusts and suspension concentrates, are described on pages 9 to 13 of WO 97/34485.

Biological Examples

Example B1: Herbicidal action prior to emergence of the plants (pre-emergence action)

Monocotyledonous and dicotyledonous test plants are sown in standard soil in plastics pots. Immediately after sowing, the test compounds, in the form of an aqueous suspension (prepared from a 25 % wettable powder (Example F3, b), as described, for example, in WO 97/34485), or in the form of an emulsion (prepared from a 25 % emulsifiable concentrate (Example F1, c), as described, for example, in WO 97/34485), are applied by spraying in a concentration corresponding to 2000 g of active ingredient/ha (500 litres water/ha). The test plants are then grown in a greenhouse under optimum conditions. After a test duration of 3 weeks, the test is evaluated in accordance with a scale of nine ratings (1 = total damage, 9 = no action). Ratings of from 1 to 4 (especially from 1 to 3) indicate good to very good herbicidal action. In this test the compounds of formula I exhibit strong herbicidal action.

Test plants: Lolium, Setaria, Sinapis, Solanum, Ipomoea

Examples of the good herbicidal activity of the compounds of formula I are given in Table B1.

Table B1: Pre-emergence action:

Test plant:	Lolium	Setaria	Sinapis	Solanum	Ipomoea	conc. [g a.i./ha]
Comp. No.						
1.002	1	1	1	1	2	2000
1.007	3	1	1	1	1	2000
1.064	3	1	1	1	1	2000
1.071	6	1	1	1	3	2000
1.074	1	1	1	1	1	2000
1.139	1	1	1	1	1	2000

The same results are obtained when compounds of formula I are formulated in accordance with Examples F2 and F4 to F8 according to WO 97/34485.

Example B2: Post-emergence herbicidal action

In a greenhouse, monocotyledonous and dicotyledonous test plants are grown in standard soil in plastics pots and at the 4- to 6-leaf stage are sprayed with an aqueous suspension of the test compounds of formula I, prepared from a 25 % wettable powder (Example F3, b) according to WO 97/34485), or with an emulsion of the test compounds of formula I, prepared from a 25 % emulsifiable concentrate (Example F1, c) according to

WO 97/34485), in a concentration corresponding to 2000 g of active ingredient/ha (500 litres water/ha). The test plants are then grown on in a greenhouse under optimum conditions. After a test duration of about 18 days, the test is evaluated in accordance with a scale of nine ratings (1 = total damage, 9 = no action). Ratings of from 1 to 4 (especially from 1 to 3) indicate good to very good herbicidal action.

Test plants: Lolium, Setaria, Sinapis, Solanum, Ipomoea

In this test too, the compounds of formula I according to the invention exhibit strong herbicidal action.

Examples of the good herbicidal activity of the compounds of formula I are given in Table B2.

Table B2: Post-emergence action:

Test plant:	Lolium	Setaria	Sinapis	Solanum	Ipomoea	conc. [g a.i./ha]
Comp. No.						
1.002	1	1	1	1	1	2000
1.007	2	2	1	1	1	2000
1.064	4	4	3	1	1	2000
1.071	2	2	1	1	3	2000
1.074	1	1	1	1	1	2000
1.139	1	1	1	1	1	2000

The same results are obtained when compounds of formula I are formulated in accordance with Examples F2 and F4 to F8 according to WO 97/34485.

The compounds of formula I according to the invention can also be used for weed control in admixture with known herbicides as co-herbicides, for example in the form of ready-prepared formulations or in the form of a 'tank-mix'. Suitable mixing partners for the compounds of formula I include, for example, the following co-herbicides: compound of formula I + acetochlor, compound of formula I + acifluorfen, compound of formula I + alachlor, compound of formula I + ametryn, compound of formula I + aminotriazole, compound of formula I + amidosulfuron, compound of formula I + asulam, compound of formula I + atrazine, compound of formula I + BAY FOE 5043, compound of formula I + benazolin, compound of formula I + bensulfuron, compound of

formula I + bentazone, compound of formula I + bifenox, compound of formula I + bispyribac-sodium, compound of formula I + bialaphos, compound of formula I + bromacil, compound of formula I + bromoxynil, compound of formula I + bromophenoxim, compound of formula I + butachlor, compound of formula I + butylate, compound of formula I + cafenstrole, compound of formula I + carbetamide, compound of formula I + chloridazone, compound of formula I + chlorimuron-ethyl, compound of formula I + chlorbromuron, compound of formula I + chlorsulfuron, compound of formula I + chlortoluron, compound of formula I + cinosulfuron, compound of formula I + clethodim, compound of formula I + clodinatop, compound of formula I + clomazone, compound of formula I + clopyralid, compound of formula I + cloransulam, compound of formula I + cyanazine, compound of formula I + cyhalofop, compound of formula I + dalapon, compound of formula I + 2,4-D, compound of formula I + 2,4-DB, compound of formula I + desmetryn, compound of formula I + desmedipham, compound of formula I + dicamba, compound of formula I + diclofop, compound of formula I + difenzoquat metilsulfate, compound of formula I + diflufenican, compound of formula I + dimefuron, compound of formula I + dimepiperate, compound of formula I + dimethachlor, compound of formula I + dimethametryn, compound of formula I + dimethenamid, compound of formula I + S-dimethenamid, compound of formula I + dinitramine, compound of formula I + dinoterb, compound of formula I + dipropetryn, compound of formula I + diuron, compound of formula I + diquat, compound of formula I + DSMA, compound of formula I + EPTC, compound of formula I + esprocarb, compound of formula I + ethalfluralin, compound of formula I + ethametsulfuron, compound of formula I + ethephon, compound of formula I + ethofumesate, compound of formula I + ethoxysulfuron, compound of formula I + fenciorim, compound of formula I + flamprop, compound of formula I + fluazasulfuron, compound of formula I + fluazifop, compound of formula I + flumetralin, compound of formula I + flumetsulam, compound of formula I + fluometuron, compound of formula 1 + flurochloridone, compound of formula 1 + fluoxaprop, compound of formula I + fluroxypyr, compound of formula I + fluthiacet-methyl, compound of formula I + fluxofenim, compound of formula I + fomesafen, compound of formula I + glufosinate, compound of formula I + glyphosate, compound of formula I + halosulfuron, compound of formula I + haloxyfop, compound of formula I + hexazinone, compound of formula I + imazamethabenz, compound of formula I + imazapyr, compound of formula I + imazaquin, compound of formula I + imazethapyr, compound of formula I + imazosulfuron, compound of formula I + ioxynil, compound of formula I + isoproturon, compound of formula I + isoxaben, compound of formula I + isoxaflutole, compound of formula I + karbutylate, compound of formula I + lactofen, compound of formula I + lenacil, compound of formula I + linuron, compound of formula I + MCPP, compound of formula I + metamitron, compound of formula I + metazachlor, compound of formula I + methabenzthiazuron, compound of formula I + methazole, compound of formula I + metobromuron, compound of formula I + metolachlor, compound of formula I + S-metolachlor, compound of formula I + metosulam, compound of formula I + metribuzin, compound of formula I + metsulfuronmethyl, compound of formula I + molinate, compound of formula I + MCPA, compound of formula I + MSMA, compound of formula I + napropamide, compound of formula I + NDA-402989, compound of formula I + nefenacet, compound of formula I + nicosulfuron, compound of formula I + norflurazon, compound of formula I + oryzalin, compound of formula I + oxadiazon, compound of formula I + oxasulfuron, compound of formula I + oxyfluorfen, compound of formula I + paraquat, compound of formula I + pendimethalin, compound of formula I + phenmedipham, compound of formula I + phenoxaprop-P-ethyl (R), compound of formula I + picloram, compound of formula I + pretilachlor, compound of formula I + primisulfuron, compound of formula I + prometon, compound of formula I + prometryn, compound of formula I + propachlor, compound of formula I + propanil, compound of formula I + propazine, compound of formula I + propaguizatop, compound of formula I + propyzamide, compound of formula I + prosulfuron, compound of formula I + pyrazolynate, compound of formula I + pyrazosulfuron-ethyl, compound of formula I + pyrazoxyphen, compound of formula I + pyridate, compound of formula I + pyriminobacmethyl, compound of formula I + pyrithiobac-sodium, compound of formula I + quinclorac. compound of formula I + quizalofop, compound of formula I + rimsulfuron, compound of formula I + sequestrene, compound of formula I + sethoxydim, compound of formula I + simetryn, compound of formula I + simazine, compound of formula I + sulcotrione, compound of formula I + sulfosate, compound of formula I + sulfosulfuron-methyl, compound of formula I + tebutam, compound of formula I + tebuthiuron, compound of formula I + terbacil, compound of formula I + terbumeton, compound of formula I + terbuthylazine, compound of formula I + terbutryn, compound of formula I + thiazafluron, compound of formula I + thiazopyr, compound of formula I + thifensulfuron-methyl, compound of formula I + thiobencarb, compound of formula I + tralkoxydim, compound of formula I + triallate, compound of formula I + triasulfuron, compound of formula I + trifluralin, compound of formula I + tribenuron-methyl, compound of formula I + triclopyr, compound of formula I + triflusulfuron, and compound of formula I + trinexapac-ethyl, and esters and salts of those mixing partners for the compound of formula I that are mentioned e.g. in The Pesticide Manual, Eleventh Edition, 1997, BCPC.

What is claimed is:

1. A compound of formula I

$$R_2$$
 N
 N
 N
 R_3
 N

wherein

R₁ is hydrogen, fluorine, chlorine, bromine or methyl;

R₂ is C₁-C₄alkyl, C₁-C₄haloalkyl, halogen, nitro, amino, cyano or R₄₃O-;

R₄₃ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, C₃-C₆cycloalkyl, C₁-C₈haloalkyl, cyano-C₁-C₈alkyl, C₃-C₈haloalkenyl, hydroxy-C₁-C₄alkyl, C₁-C₄alkoxy-C₁-C₄alkyl, C₃-C₆-alkenyloxy-C₁-C₄alkyl, C₃-C₆alkynyloxy-C₁-C₄alkyl, C₁-C₄alkoxy-C₁-C₄alkoxy-C₁-C₄-alkyl, C₁-C₄alkylthio-C₁-C₄alkyl, C₁-C₈alkylcarbonyl, C₁-C₈alkoxycarbonyl, C₃-C₈alkenyloxycarbonyl, benzyloxy-C₁- or -C₂-alkyl, benzylcarbonyl, benzyloxycarbonyl, phenyl, phenyl-C₂-C₈alkyl, benzyl, pyridyl, pyrimidinyl, pyrazinyl or pyridazinyl, those aromatic and heteroaromatic rings being unsubstituted or mono- to tri-substituted by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl; or

 X_{16} is oxygen, sulfur or $R_{\overline{45}} N -$;

R₄₄ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, C₃-C₆cycloalkyl, C₁-C₈haloalkyl, C₃-C₈haloalkenyl, C₁-C₄alkoxy-C₁-C₄alkyl, C₃-C₆alkenyloxy-C₁-C₄alkyl, C₁-C₄alkylthio-C₁-C₄alkyl, phenyl mono- to tri-substituted by halogen, C₁-C₄alkyl or by C₁-C₄-haloalkyl, benzyl or benzyl mono- to tri-substituted on the phenyl ring by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl;

R₄₅ is hydrogen, C₁-C₈alkyl, C₃-C₈alkenyl, C₃-C₈alkynyl, C₃-C₆cycloalkyl, C₁-C₈haloalkyl or benzyl;

R₃ is hydroxy, C₁-C₆alkoxy, C₃-C₆alkenyloxy, C₃-C₆alkynyloxy, C₁-C₆haloalkoxy, C₃-C₆haloalkoxy, C₃-C₆haloalkenyloxy, C₁-C₆alkoxy-C₁-C₆alkyl, C₃-C₆alkynyloxy-C₁-C₆alkyl, C₁-C₆alkoxy-C₁-C₆alkoxy-C₁-C₆alkyl, B₁-C₁-C₆alkoxy, R₄(R₅)N-, C₁-C₆alkyl, C₃-C₆alkenyl, C₃-C₆alkynyl, C₂-C₆haloalkyl, C₃-C₆haloalkenyl, C₃-C₆cycloalkyl, C₃-C₆haloalkyl, B₁-C₁-C₆alkyl, OHC-, C₁-C₆alkylcarbonyl, C₁-C₆alkylcarbonyl, C₁-C₆alkylcarbonyl, C₁-C₆alkylcarbonyl, C₁-C₆alkylcarbonyl, C₁-C₆alkyl-S(O)₂-,

$$C_1-C_6 \\ haloalkyl-S(O)_2-, \ C_3-C_8 \\ trialkylsilyloxy, \ (C_1-C_6 \\ alkyl)_2 \\ N-N=CH-, \quad \bigcap_{O} \\ CH_2- \quad ,$$

$$O \leftarrow C_1$$
- C_3 alkyl , B₁-CH=N-, (CH₃)₂N-CH=N-, (C₁-C₅hydroxyalkyl)-CH₂-, (B₁-C₁-C₅-CH₂-

hydroxyalkyl)- CH_2 -, (B_1 - C_1 - C_5 haloalkyl)- CH_2 -, (hydroxy- C_1 - C_5 alkyl)-O- or (B_1 - C_1 - C_5 -hydroxyalkyl)-O-;

- B₁ is cyano, OHC-, HOC(O)-, C₁-C₆alkylcarbonyl, C₁-C₆haloalkylcarbonyl, C₁-C₆alkoxy-carbonyl, C₃-C₆alkenyloxycarbonyl, C₃-C₆alkynyloxycarbonyl, benzyloxy, benzyloxy-carbonyl, benzyloxycarbonyl mono- to tri-substituted on the phenyl ring by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl, benzylthio, benzylthiocarbonyl, benzylthiocarbonyl mono- to tri-substituted on the phenyl ring by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl, C₁-C₆haloalkoxycarbonyl, C₁-C₆alkylthio-C(O)-, R₆(R₇)NC(O)-, phenyl, phenyl mono- to tri-substituted by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl, C₁-C₆alkyl-S(O)₂-, C₁-C₆alkyl-S(O)-, C₁-C₆alkylthio-, C₃-C₆cycloalkyl, C₁-C₆alkoxy, C₃-C₆alkenylthio or C₃-C₆-alkynylthio;
- R₄ and R₅ are each independently of the other hydrogen, C₁-C₆alkyl, C₃-C₆alkenyl, C₃-C₆-alkynyl, C₁-C₆haloalkyl, C₃-C₆haloalkenyl, C₃-C₆cycloalkyl, C₁-C₆alkoxy-C₁-C₆alkyl, OHC-, C₁-C₆alkylcarbonyl, C₁-C₆haloalkylcarbonyl, C₁-C₆alkyl-S(O)₂- or C₁-C₆haloalkyl-S(O)₂-;
- R₆ and R₇ are each independently of the other hydrogen, C₁-C₆alkyl, C₃-C₆alkenyl, C₃-C₆-alkynyl, C₁-C₆haloalkyl, C₃-C₆haloalkenyl, phenyl mono- to tri-substituted by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl, benzyl or benzyl mono- to tri-substituted on the phenyl ring by halogen, C₁-C₄alkyl or by C₁-C₄haloalkyl;
- X_1 is oxygen or sulfur;

W is a group
$$R_{10}$$
 R_{10} R_{10} R_{10} R_{10} R_{10} R_{10} R_{10} R_{10} R_{11} R_{11} R_{11} R_{11} R_{11} R_{12} R_{12} R_{13} R_{14} R_{14} R_{15} R_{14} R_{15} R_{14} R_{15} R_{15} R_{16} R_{16}

$$X_{12}$$
 X_{11} X_{13} X_{14} X_{14} X_{15} X

R₈ is C₁-C₃alkyl, C₁-C₃haloalkyl or amino;

 R_9 is C_1 - C_3 haloalkyl, C_1 - C_3 alkyl- $S(O)_{n1}$, C_1 - C_3 haloalkyl- $S(O)_{n1}$ or cyano; or

R₈ and R₉ together form a C₃- or C₄-alkylene bridge or C₃- or C₄-alkenylene bridge, each of which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

 n_1 is 0, 1 or 2;

R₁₀ is hydrogen, C₁-C₃alkyl, halogen, C₁-C₃haloalkyl or cyano; or

R₁₀ and R₉ together form a C₃- or C₄-alkylene bridge or C₃- or C₄-alkenylene bridge, each of which may be substituted by halogen, C₁-C₃haloalkyl or by cyano;

R₁₁ is hydrogen, C₁-C₃alkyl, halogen or cyano;

 R_{12} is C_1 - C_3 haloalkyl;

R₁₂ and R₁₁ together form a C₃- or C₄-alkylene bridge or C₃- or C₄-alkenylene bridge;

R₁₃ is hydrogen, C₁-C₃alkyl or halogen;

R₁₃ and R₁₂ together form a C₃- or C₄-alkylene bridge or C₃- or C₄-alkenylene bridge;

 $R_{14} \text{ is hydrogen, } C_1\text{-}C_3\text{alkyl, halogen, } C_1\text{-}C_3\text{haloalkyl, } R_{33}\text{O-, } R_{34}\text{S}(\text{O})_{n2}, \ R_{35}(R_{36})\text{N, }$

 $R_{38}(R_{39})N-C(R_{37})=N-$, hydroxy, nitro or $N\equiv C-S-$;

 R_{33} is C_1 - C_3 alkyl, C_1 - C_3 haloalkyl, C_2 - C_4 alkenyl, C_3 - or C_4 -alkynyl or C_1 - C_5 alkoxycarbonyl- C_1 - C_4 alkyl;

R₃₄ is C₁-C₄alkyl or C₁-C₄haloalkyl;

 n_2 is 0, 1 or 2;

R₃₅ is hydrogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₃-C₆cycloalkyl, OHC- or C₁-C₄alkylcarbonyl;

R₃₆, R₃₇ and R₃₉ are each independently of the others hydrogen or C₁-C₄alkyl;

R₃₈ is C₁-C₄alkyl;

R₁₅ is hydrogen, C₁-C₄alkyl, halogen, C₁-C₄haloalkyl, C₂-C₄alkenyl, C₃-C₅haloalkenyl, C₃-or C₄-alkynyl, C₁-C₄alkoxy, C₁-C₄alkylcarbonyl, C₁-C₄haloalkylcarbonyl, C₂-C₄alkenylcarbonyl, C₂-C₄haloalkenylcarbonyl, C₂-C₄haloalkynylcarbonyl, C₁-C₄alkynylcarbonyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₃-O₄-Alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₃-O₄-Alkylcarbamoyl, C₁-C₄alkylcarbamoyl, C₂-C₄alkylcarbamoyl, C₃-O₄-Alkylcarbamoyl, C

n₃ is 0, 1 or 2;

R₁₆ and R₁₇ are each independently of the other hydrogen, C₁-C₄alkyl, halogen, C₁-C₄halo-alkyl or cyano;

 R_{18} and R_{19} are each independently of the other hydrogen, methyl, halogen, hydroxy or =0; R_{20} and R_{21} are each independently of the other hydrogen, C_1 - C_4 alkyl or C_1 - C_4 haloalkyl; R_{22} and R_{23} are each independently of the other hydrogen, C_1 - C_3 alkyl, halogen or hydroxy; R_{24} and R_{25} are each independently of the other hydrogen or C_1 - C_4 alkyl; or

$$R_{24}$$
 and R_{25} together form the group $=C\begin{bmatrix} R_{40} \\ R_{41} \end{bmatrix}$;

R₄₀ and R₄₁ are each independently of the other C₁-C₄alkyl; or

R₄₀ and R₄₁ together form a C₄- or C₅-alkylene bridge;

R₂₆ is hydrogen or C₁-C₃alkyl; or

R₂₆ together with R₂₅ forms a C₃-C₅alkylene bridge, which may be interrupted by oxygen and/or substituted by halogen, C₁-C₄alkyl, C₂-C₄alkenyl, C₁-C₃haloalkyl, C₁-C₃alkyl-carbonyloxy, C₁-C₄alkoxycarbonyl, C₁-C₃alkylsulfonyloxy, hydroxy or by =O;

R₂₇, R₂₈, R₂₉ and R₃₀ are each independently of the others hydrogen, C₁-C₃alkyl, C₃- or C₄-alkenyl or C₃-C₅alkynyl; or

R₂₇ and R₂₈ together and/or R₂₉ and R₃₀ together in each case form a C₂-C₅alkylene bridge or C₃-C₅alkenylene bridge, each of which may be interrupted by oxygen, sulfur or - S(O)₂- and/or substituted by halogen, C₁-C₄alkyl, C₂-C₄alkenyl, C₁-C₃alkylcarbonyloxy, C₁-C₃alkylsulfonyloxy, hydroxy or by =O;

R₃₁ is hydrogen, C₁-C₄alkyl, C₁-C₄haloalkyl, C₃- or C₄-alkenyl, C₃- or C₄-haloalkenyl or C₃- or C₄-alkynyl;

R₃₂ is hydrogen, C₁-C₄alkyl, C₁-C₃alkoxy-C₁- or -C₂-alkyl, C₁-C₄haloalkyl, C₃- or C₄-alkenyl, C₃- or C₄-alkynyl; or

R₃₂ and R₃₁ together form a C₃-C₅alkylene bridge; and

 X_2 , X_3 , X_4 , X_5 , X_6 , X_7 , X_8 , X_9 , X_{10} , X_{11} , X_{12} , X_{13} , X_{14} and X_{15} are each independently of the others oxygen or sulfur,

or an agrochemically acceptable salt or stereoisomer of such a compound of formula I.

2. A compound according to claim 1 of formula lo

$$R_2 \xrightarrow{R_1} W \qquad (I_0),$$

$$X_1 \qquad R_3$$

wherein R_1 is hydrogen, fluorine, chlorine, bromine or methyl; R_2 is methyl, halogen, hydroxy, nitro, amino or cyano; and R_3 , X_1 and W are as defined in claim 1.

3. A process for the preparation of a compound of formula I

wherein R_1 , R_2 and W are as defined in claim 1; X_1 is O or S; R_3 is C_1 - C_6 alkoxy- C_1 - C_6 alkyl, C_1 - C_6 alkoxy- C_1 - C_6 alkyl, C_3 - C_6 alkenyl, C_3 - C_6 alkynyl, C_2 - C_6 haloalkyl,

$$O \xrightarrow{C_1-C_3 alkyl} , \ (C_1-C_5 hydroxyalkyl)-CH_2-, \ (B_1-C_1-C_5 hydroxyalkyl)-CH_2- \ or \ CH_2-$$

 $(B_1-C_1-C_5haloalkyl)-CH_2-$; and B_1 is as defined in claim 1, which process comprises oxidising a compound of formula III

$$R_2 \longrightarrow W$$
 (III)

in a suitable solvent to form a compound of formula V

$$R_2 \xrightarrow{R_1} W \qquad (V)$$

and then rearranging that compound in an inert solvent in the presence of an anhydride or in the presence of antimony pentachloride to yield, after aqueous working-up, a compound of formula II

$$R_2$$
 \longrightarrow W (II),

the radicals R₁, R₂ and W in the compounds of formulae II, III and V being as defined, and then alkylating that compound in the presence of an inert solvent and a base with a compound of formula VI

$$R_3$$
-L (VI),

wherein R_3 is as defined and L is a leaving group, in a suitable inert solvent and a base to form the compounds of formulae I and IV

wherein R_1 , R_2 , R_3 and W are as defined and X_1 is O, and then, after the compound of formula I has been separated from the pyridol derivative of formula IV, optionally functionalising the pyridono derivative of formula I further in accordance with the definitions of X_1 and R_3 .

4. A compound of formula II

wherein R₁, R₂ and W are as defined in claim 1.

- 5. A herbicidal and plant-growth-inhibiting composition, comprising a herbicidally effective amount of a compound of formula I on an inert carrier.
- 6. A herbicidal and plant-growth-inhibiting composition according to claim 5, comprising at least one further co-herbicide as additional component.
- 7. A method of controlling undesired plant growth, which method comprises applying a compound of formula I, or a composition comprising such a compound, in a herbicidally effective amount to plants or to the locus thereof.
- 8. Use of a composition according to claim 5 in the control of undesired plant growth.

Int. .ional Application No

		PCI/EF 99	7/ 02313
IPC 6	FICATION OF SUBJECT MATTER C07D401/04 A01N43/54 A01N43/5 A01N43/653	8 A01N43/56 A01N	143/50
According to	o International Patent Classification (IPC) or to both national classifica	ation and IPC	
B. FIELDS	SEARCHED		
Minimum do IPC 6	cumentation searched (classification system followed by classification COTD A01N	on symbols)	
	tion searched other than minimum documentation to the extent that s		
	ata base consulted during the international search (name of data bas	se and, where practical, search terms use	d)
	ENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the rele	evant passages	Relevant to claim No.
P,A	WO 98 55480 A (COLLINS IAN JAMES STEPHEN ROBERT (GB); LEESON PAUL 10 December 1998 (1998-12-10) claim 1	;FLETCHER DAVID)	1-8
A	US 5 726 124 A (ROEMMELE RENEE CA ET AL) 10 March 1998 (1998-03-10) column 2, line 5 - column 5, lir)	1-8
А	DE 195 30 606 A (BASF AG) 27 February 1997 (1997-02-27) cited in the application claim 1		1-8
А	DE 195 18 054 A (HOECHST SCHERING GMBH) 12 September 1996 (1996-09-cited in the application claim 1		1-8
X Funt	her documents are listed in the continuation of box C.	γ Patent family members are lister	d in annex.
° Special ca	ategories of cited documents :		
"A" docume consid	ent defining the general state of the art which is not dered to be of particular relevance document but published on or after the international	"T" later document published after the into or priority date and not in conflict with cited to understand the principle or trinvention "X" document of particular relevance; the	h the application but heory underlying the
"L" docume which citation "O" docume other	ant which may throw doubts on priority claim(s) or is cited to establish the publication date of another in or other special reason (as specified) ent referring to an oral disclosure, use, exhibition or means ent published prior to the international filing date but	cannot be considered novel or cannot involve an inventive step when the document of particular relevance; the cannot be considered to involve an idocument is combined with one or no ments, such combination being obvi in the art.	ocument is taken alone claimed invention nventive step when the nore other such docu-
later tr	nan the priority date claimed	"&" document member of the same pater	
	actual completion of the international search	Date of mailing of the international se	earch report
	August 1999	13/09/1999	
Name and r	mailing address of the ISA European Patent Office, P.B. 5818 Patentiaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo ni, Fax: (+31-70) 340-3016	Authorized officer Gettins, M	

Int. ional Application No
PCT/EP 99/02313

		PCT/EP 99/02313
	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 07857 A (NISSAN CHEMICAL IND LTD; KAWAMURA YASUO (JP); OYA EIICHI (JP); ITO) 14 April 1994 (1994-04-14) claims 1,4	1-8
A	EP 0 500 209 A (RHONE POULENC AGROCHIMIE) 26 August 1992 (1992-08-26) cited in the application claim 1	1-8
A	DE 39 17 469 A (BAYER AG) 6 December 1990 (1990-12-06) cited in the application claim 1	1-8
А	US 4 776 976 A (NAKAMURA TOHRU ET AL) 11 October 1988 (1988-10-11) column 1, line 30 - column 2, line 50	1-8
A	PATENT ABSTRACTS OF JAPAN vol. 008, no. 056 (C-214), 14 March 1984 (1984-03-14) & JP 58 213776 A (ISHIHARA SANGYO KK), 12 December 1983 (1983-12-12) cited in the application abstract	1-8

1

Information on patent family members

Into ional Application No
PCT/EP 99/02313

	ent document in search report		Publication date		tent family ember(s)	Publication date
WO S	9855480	Α	10-12-1998	AU	7668798 A	21-12-1998
	5726124	A	10-03-1998	US AUU BRA CN EPU DX AUR	5453414 A 5300477 A 697648 B 8181294 A 9500248 A 2140182 A 1109879 A 0663396 A 70087 A 7278119 A 270297 A 28936 A 9500348 A 144500 T 4178193 A 9302896 A 2099925 A 1084165 A 69305587 D 579424 T 0579424 A 0696588 A 2093929 T 3021451 T 7797 A 65082 A 6312980 A 133083 B 248090 A 960437 A	26-09-1995 05-04-1994 15-10-1998 27-07-1995 17-10-1995 19-07-1995 11-10-1995 19-07-1995 28-09-1995 24-10-1995 24-11-1997 06-08-1997 18-07-1995 15-11-1996 20-01-1994 16-02-1994 18-01-1994 23-03-1994 28-11-1996 19-01-1994 14-02-1996 01-01-1997 31-01-1997 24-01-1997 24-01-1997 28-04-1994 08-11-1994 14-04-1998 27-02-1996 21-06-1994
DE	1953 06 06	A	27-02-1997	ZA AU CA WO EP	9305033 A 6742996 A 2226765 A 9707114 A 0846113 A	17-01-1994
DE	19518054	A	12-09-1996	NONE		
WO	9407857	Α	14-04-1994	JP AU CN	6172306 A 4834693 A 1085218 A	21-06-1994 26-04-1994 13-04-1994
EP	0500209	A	26-08-1992	AT AU BG BG CA CN CS DE DE DK EG	158290 T 644259 B 1025192 A 61813 B 95776 A 2059088 A 1063283 A,B 1208036 A 9200130 A 69222202 D 69222202 T 500209 T 19658 A	15-10-1997 02-12-1993 28-01-1993 30-06-1998 24-03-1994 19-07-1992 05-08-1992 17-02-1999 16-09-1992 23-10-1997 19-02-1998 04-05-1998 30-09-1995

Information on patent family members

inte .onal Application No
PCT/EP 99/02313

Patent document cited in search repor	t	Publication date		Patent family member(s)	Publication date
EP 0500209	A	I	ES	2106821 T	16-11-1997
			FI	920221 A	19-07-1992
			GR	3025572 T	31-03-1998
			IL	100678 A	19-01-1996
			JP	5086054 A	06-04-1993
			MX	9200182 A	01-10-1992
			NO	179282 B	03-06-1996
			NZ	241314 A	27-09-1994
			OA	9756 A	30-11-1993
			PL	168730 B	29-03-1996
			RO	109940 A	28-07-1995
			RU	2088580 C	27 -0 8-1997
			TR	25675 A	01-07-1993
			US	5306694 A	26-04-1994
			ZW	1192 A	05-08-1992
DE 3917469	Α	06-12-1990	NONE		
US 4776976	Α	11-10-1988	JP	1667810 C	29-05-1992
			JP	3033376 B	16-05-1991
			JP	62258731 A	11-11-1987
			AT	48093 T	15-12-1989
			CA	1296966 A	10-03-1992
			EP	0245756 A	19-11-1987
			HK	33491 A	10-05-1991
			PH	23642 A	27-09-1989
JP 58213776	Α	12-12-1983	NONI		